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# REPORT

ON

# SERIES IN LINE SPECTRA.

BY

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# PREFACE.

ALTHOUGH the spectra of elements and compounds were studied in the first instance chiefly as providing a powerful means of chemical analysis, it has long been recognised that a spectrum must contain an important clue to the structure and modes of vibration of the atoms or molecules which produce it. Spectra, however, are most frequently very complex, and there could be but little hope of progress in the direction indicated if it were not possible to discover laws governing the distribution of the lines or bands of which they are composed. The search for such laws has attracted many workers, and organised systems of lines which can be approximately represented by simple formulæ have been identified in the spectra of many elements and compounds. The recognition of these regularities has naturally played a fundamental part in the development of theories of the origin of spectra and of the constitution of atoms and molecules. The analysis of spectra has thus become one of the main objects of modern spectroscopy, stimulating the experimentalist to the extension of existing data, and providing material in a form suitable for the theoretical investigator.

My purpose in the present report has been to give a comprehensive account of the development and present state of our knowledge of the regularities in spectra, as deduced from the spectra themselves, with but little regard to theories of their origin. The report is in two parts, the first of which gives a general account of spectral series, excluding those which occur in band spectra, while the second is intended to include the most authentic experimental data available in April, 1921. It is hoped that the tables of series lines, together with the references to lines which have not yet been classified, will suggest and facilitate further investigations. The system of numeration of the series lines which has been adopted is that of Rydberg and Hicks, but if it should be found convenient to modify this numeration on theoretical grounds there should be no difficulty in making the desired alterations.

The spectra dealt with are those obtained by optical methods, extending from the infra-red to the extreme ultra-violet. The emissions of higher frequencies which have been revealed in the study of X-ray spectra do not form extended series of the kind met with in optical spectra, and have accordingly not been considered.

I am indebted to Professor F. A. Saunders, of Harvard University, for much useful help during the preparation of the report, and especially for his kindness in supplying important observational material in advance of publication. My thanks are also due to Col. E. H. Grove-Hills, F.R.S., for the photograph reproduced in Fig. 6; to Dr. A. S. King, of the Mount Wilson Observatory, for Plate III. *b*; and to Mr. N. R. Fowler for the negatives from which Plate IV. was prepared. I also have pleasure in acknowledging the valuable assistance which has been rendered by Dr. D. Owen, Secretary of the Physical Society, and Mr. H. Dingle, B.Sc., D.I.C., in reading the proof sheets.

A. FOWLER.

IMPERIAL COLLEGE,
SOUTH KENSINGTON, LONDON.
*February*, 1922.

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PART I.

# GENERAL ACCOUNT OF SERIES.

# CHAPTER I.

## OBSERVATIONAL DATA.

### WAVE-LENGTHS AND WAVE-NUMBERS.

The study of spectral series calls for a precise acquaintance with the nature of the available data, both as to the positions and characters of the lines involved.

The position of a line in the spectrum is most generally indicated by the wave-length ($\lambda$) of the vibrations which produce it. The unit of wave-length is the Ångström Unit, or "angstrom," as it is now beginning to be called. It was intended to equal $10^{-10}$ metre, and is accordingly often called the "tenth-metre." It is also equivalent to $10^{-8}$ cm., or $0{\cdot}0001\mu$, where $\mu$ is the micron, or thousandth of a millimetre. Wave-lengths in the visible spectrum range from about 3,900A to 7,600A (A being the modern abbreviation for the angstrom). For the long waves in the infra-red, however, $\mu$ is often taken as the unit, so that $\lambda$12,500A, for example, would be indicated by $1{\cdot}25\mu$.

The wave-length scale was introduced by Ångström in 1869, and until about the year 1900, wave-lengths were referred to his determinations as standards; they were meant to represent the wave-lengths in air at 16°C. and 760mm. pressure. Later work, however, proved that Ångström's values were about 1A too low, and, about 1896, the scale was superseded by that of Rowland, which referred to wave-lengths in air at 20°C. and 760mm. Still more recently it has been found that Rowland's scale was based upon erroneous values for the *D* lines of sodium, besides being affected by other small errors, and Rowland's scale is now being gradually replaced by the "International" scale. The latter is founded upon interferometer determinations of the wave-length of the red line of cadmium, which is much superior to the sodium lines in point of sharpness. The wave-length adopted for this line by the International Solar Union* is 6438·4696, being the value determined by Benoit, Fabry, and Perot, and in close accordance with a previous measurement by Michelson. The precision of this value for the standard line is such that the unit of wave-length which it defines can differ but little from $10^{-10}$m., but to avoid all misunderstanding the unit of wave-length defined by the cadmium line has been called the International Angstrom; and is indicated in tables by the letters "*I.A.*"; we thus have

$$I.A. = \frac{\text{Wave-length of red Cd line in dry air at 15°C., 760 mm., with } g = 980{\cdot}67}{6438{\cdot}4696}$$

The majority of published wave-lengths, however, have been expressed on Rowland's scale, and if new determinations have not become available, it is necessary to reduce the Rowland values to the international scale in any precise work on series. From a comparison of the two scales, Kayser † has derived the corrections which are shown in Table I. These corrections include the small differences depending upon the differences in the standard temperatures of the two scales (20°C. for Rowland, and 15°C. for the international scale).

In connection with spectral series it becomes important to specify the positions

* Trans. Int. Sol. Union, **2**, 20, 28 (1907). (The Solar Union is now absorbed into the International Astronomical Union.)

† Handbuch der Spectroscopie, **6**, 891 (1912).

of lines either in "oscillation-frequencies," or by "wave-numbers." The most fundamental figures are the oscillation-frequencies, since these are not changed when the medium is changed. But the determination of frequency requires an exact knowledge of the velocity of light, and it is more convenient to use the wave-number, or number of waves per centimetre; thus—

$$\text{Wave-number} = \nu = \frac{10^8}{\lambda \text{ in angstroms}}$$

### Correction to Vacuum.

Wave-numbers as well as wave-lengths vary with the medium in which the vibrations are propagated, and it is therefore necessary to reduce them to standard conditions. They are accordingly reduced to their values *in vacuo*, and when thus corrected the wave-numbers are strictly proportional to the oscillation-frequencies. This correction can be made when the refraction and dispersion of air have been determined with sufficient accuracy. Thus—

$$\lambda_{vac.} = \mu\lambda_{air}; \text{ or } \Delta\lambda = \lambda_{vac.} - \lambda_{air} = \lambda_{air}(\mu - 1)$$

where $\mu$=the refractive index of air.

The refractive index, of course, varies with the density, and therefore with the temperature and pressure, of the air. Kayser and Runge have given a formula indicating the value of $\mu$ for air at 760mm. pressure, and temperature 0°C., and have derived a table of corrections to vacuum applicable to wave-lengths determined in air at 20°C. and 760mm. pressure.* The most recent observations have been made at the Washington Bureau of Standards by Meggers and Peters,† who give the following formulæ for the refractive indices of dry air at 760mm. pressure, and temperatures 0°C., 15°C. and 30°C., $\lambda$ being expressed in angstroms :—

$$0°\text{C.}: \ (\mu-1)_0 \times 10^7 = 2875{\cdot}66 + \frac{13{\cdot}412}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}3777}{\lambda^4 \times 10^{-16}}$$

$$15°\text{C.}: \ (\mu-1)_{15} \times 10^7 = 2726{\cdot}43 + \frac{12{\cdot}288}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}3555}{\lambda^4 \times 10^{-16}}$$

$$30°\text{C.}: \ (\mu-1)_{30} \times 10^7 = 2589{\cdot}72 + \frac{12{\cdot}259}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}2576}{\lambda^4 \times 10^{-16}}$$

These observations have been utilised in the construction of a table showing the corrections which must be applied to wave-lengths and wave-numbers measured in air to convert them to their values in vacuum. An extract from the Washington tables is given in Table II., indicating the amounts to be added to wave-lengths in dry air at 15°C. and 760mm., and therefore directly applicable to wave-lengths on the international scale.‡ The conversion to wave-numbers can readily be effected by the use of a table of reciprocals with seven-place arguments.

When the wave lengths are expressed on Rowland's scale, which refers to 20°C., the simplest procedure is to reduce them to the international system by means of

* Handbuch, 2, 514.

† Scientific Papers of the Bureau of Standards, Washington, No. 327 (1918).

‡ Some of the figures have been slightly amended in Astrophys. Jour., 50, 56 (1919).

Table I., and then to correct them to vacuum by adding the corrections given in Table II.

The corrections of infra-red wave-lengths to the international system and to vacuum are subject to some uncertainty. For wave-lengths greater than 10,000A, however, the correction to the international scale has but little influence on the wave-numbers. Thus, at λ10,000 the correction increases the wave-number by 0·4, at λ20,000 by 0·2, and at λ40,000 by 0·1. Corrections to vacuum may be determined approximately by extrapolation of the Washington formula for the refractive index of air. (*See* Table II*a*.)

### Arc and Spark Spectra: Enhanced Lines.

The investigation of spectral series often requires a knowledge of the behaviour of the lines when produced under different conditions of excitation. The spectra of metallic elements are most frequently obtained by the use of the electric arc or by the condensed discharge from an induction coil, and the spectrum is usually different in the two cases. (*See* Plate IV.) On passing from the arc to the spark it often happens that some of the lines are diminished in relative intensity, while others become brighter, and new lines frequently make their appearance in the spark. Lines which are relatively enhanced in brightness on passing from the arc to the spark, or which only occur in the spark spectrum, were called *Enhanced Lines* by Lockyer, and this name has been generally adopted. Lines which appear in the arc and tend to diminish in intensity in the spark are then distinguished as *Arc Lines*. The term "arc lines," it will be seen, does not necessarily include *all* the lines which appear in the arc spectrum; and, similarly, the spark spectrum most frequently includes some surviving arc lines as well as enhanced lines.

It is convenient to distinguish at least three classes of enhanced lines: (I.) Enhanced lines like the *H* and *K* lines of calcium, which are quite strong in the arc (and appear with greater intensity in the spark); (II.) Lines which only appear with feeble or moderate intensity in the ordinary arc, such as the enhanced lines of iron and titanium; (III.) Lines which do not appear in the ordinary arc, but are strongly developed under spark conditions, as in the case of the well-known magnesium line λ4,481. It would thus seem that while the energy of the arc is in some cases sufficient to develop the enhanced lines, the greater energy of the disruptive spark is required to give rise to them in the case of some of the elements. In other words, different elements respond differently to a given stimulus.

It should be mentioned that enhanced lines are also often found to appear in a region close to the poles of a metallic arc, and when the arc is passed in an atmosphere of hydrogen, or in a vacuum,* they frequently become very pronounced.

Similar variations of the line spectrum are also observed in the case of many gases, including helium, oxygen, and nitrogen, when the electric discharges which excite them are varied in intensity. From analogy with metallic spectra, certain lines which thus appear in the spectra of gases under the action of powerful discharges may quite properly be classed as enhanced lines. In some cases, a succession of spectra appear as the intensity of the discharge is gradually increased. Oxygen, for example, gives a spectrum corresponding to the arc spectrum when the discharge is feeble, new lines appear with a moderate increase in the intensity, and still others when the strongest discharges are passed through the gas; the three

* Fowler and Payn, Proc. Roy. Soc., **72**, 253 (1903).

different classes of lines are then conveniently distinguished as arc, spark and "super-spark," or as *O*I., *O*II., and *O*III.* Silicon shows four such stages.

As might be expected, arc lines and enhanced lines have not been found to be associated in the same family of series.

## Intensities and Characters of Lines.

In the investigation of series spectra, it is important also to take into account the intensities and physical characteristics of the lines involved. A convenient standard scale of intensities has not yet been introduced into spectroscopic tables, and tabulated intensities are, for the most part, merely rough estimates on an arbitrary scale, in which 10 represents the strongest and 1 the weakest lines. This range, however, is often too restricted, and in some tables, notably those of Exner and Haschek, the very strongest lines are represented by the higher numbers 15, 20, 30, 50, 100, 200, 500 and 1,000. In order to extend the scale in the opposite direction, some observers also follow Rowland's convenient plan of indicating very faint lines by 0, 00, 000, and 0000, the latter being at the limit of visibility. A method of estimating intensities on an absolute scale has been devised by Nicholson and Merton,† but its use has so far been restricted to the spectrum of helium.

While some lines are sharp and well-defined, others may be shaded on one or both edges, and others again, especially in arc spectra, may be reversed. These different appearances are usually indicated in spectroscopic tables by the addition of letters to the numbers showing the intensities. There is, unfortunately, a considerable diversity in the notations adopted by different observers, and it is usually necessary to rely upon an author to describe the symbols employed in any particular case. Some of the principal systems which have been adopted are as follows :—

| Character. | Watts. | Kayser. | Exner and Haschek. | This Report. |
|---|---|---|---|---|
| Sharp | *s* | *s** | — | *s* |
| Nebulous or diffuse | *n* | *u*† | + | *n* |
| Broad | *b* | *u*† | *br*‡ | *b* |
| Broad, but sharp on red edge | $b^r$ | — | — | — |
| Diffuse towards violet | — | *v*, or *uv* | *v* | *v* |
| Broad, but sharp on violet edge | $b^v$ | — | — | — |
| Diffuse towards red | — | *r*, or *ur* | *r* | *r* |
| Reversed | *r* | *R* | *u*§ | *R* |
| Double | — | *d* | *d* | *d* |

* Scharf. † Unscharf. ‡ Breit. § Umgekehrt.

The symbols in the last column will be adopted in this report, and it is to be understood that the absence of any symbol indicates that the line is of ordinary sharpness, but not specially sharp.

In a reversed line there is a broad bright line, diffuse at the edges, which is produced by the denser vapour at the core of the arc or spark used as the source of light, and a narrow absorption line superposed upon this which originates in the cooler and less dense vapour in the outer envelope. The reversal is sometimes unsymmetrical.

* Fowler and Brooksbank, Monthly Notices, R.A.S., **77**, 511 (1917).
† Phil. Trans., A, **217**, 242.

It should be noted that lines which are ordinarily diffuse in an arc spectrum can usually be obtained as sharp lines by passing the arc in a vacuum. There are, in fact, examples of series which might never have been recognised as such if reliance had been placed upon observations of the arc or spark in air, as the more refrangible members are sometimes diffused to the degree of invisibility.

Lines which belong to the same series are usually similar in character, but an apparent exception has been noted by Royds in barium ;* in this case the lines of a triplet in the yellow appear to be widened unsymmetrically towards the red, while the more refrangible triplets are shaded towards the violet. The corresponding triplets of calcium present a less extreme exception, the blue triplet being sharply defined, while succeeding members are diffuse towards the violet; the associated infra-red triplet may possibly be shaded towards the red.

### The Schumann and Infra-Red Regions.

The ordinary instruments which are employed in spectroscopic work do not permit the investigation of the whole range of the spectrum. Spectroscopes with prisms and lenses of glass only serve for a small part of the ultra-violet, and a small part of the infra-red, in addition to the visible spectrum. When quartz is substituted for glass the range may be extended to about $\lambda$1,850 in the ultra-violet, but for shorter wave-lengths special arrangements become necessary. This part of the spectrum was first investigated by Schumann, and is commonly called the Schumann region. In the first instance, fluorite was substituted for quartz, and on account of the opacity of air for the short waves the whole apparatus, including the photographic plate, was placed in an exhausted air-tight case. The ordinary gelatine plates being strongly absorbent for short waves, special " Schumann plates " with a very thin coating of gelatine are also necessary. Concave gratings have been successfully employed by Lyman and others, and have permitted observations beyond the region for which fluorite is transparent. Details of the instruments and methods of work have been given by Lyman in his book on " The Spectroscopy of the Extreme Ultra-Violet."†

Observations have now been extended as far as $\lambda$ 584A by McLennan‡ and to 220A by Millikan.§ Wave-lengths in this region are usually tabulated as observed, and no correction to vacuum is required in the calculation of wave-numbers. It should be noted that since $d\nu = -10^8/\lambda^2 . d\lambda$, errors in the wave-length are greatly multiplied in the conversion to wave-numbers in this region as compared with the less refrangible parts of the spectrum.

At the red end of the spectrum, direct photographs on plates stained with dicyanin have been obtained by Meggers as far as $\lambda$10,000A.‖ The further infra-red is investigated by thermo-electric methods, employing spectroscopes having optical parts of rock-salt or making use of gratings. Extensive work with special reference to series lines has been carried on in this region by Paschen¶ and by Randall.**

The extension of observations into the extreme ultra-violet and infra-red has been of great value in the elucidation of the structure of spectral series, as will appear in due course.

* Astrophys. Jour., **41**, 154 (1914).
† Longmans (1914).
‡ McLennan, Proc. Roy. Soc., A., **95**, 238 (1919).
§ Astrophys. Jour., **52**, 47 (1920).
‖ Scientific Papers of the Bureau of Standards, Washington. Numbers 312, 324, 345, &c.
¶ Ann. d. Phys., (4) **27**, **29**, **33** (1908-10), and other Papers.
** Astrophys. Jour., **34**, 1 (1911) ; **42**, 195 (1915) ; **49**, 42, 54 (1919).

## SOURCES OF DATA.

The following references to the principal collected tables of wave-lengths and photographs of spectra may be usefully appended to this chapter.

(1) W. MARSHALL WATTS: "Index of Spectra," with numerous appendices. (Heywood, Manchester.)

(2) F. EXNER and E. HASCHEK: "Wellenlängen Tabellen für Spectralanalytische Untersuchungen auf Grund der Ultra-Violetten Funkenspektren der Elemente." (Leipzig and Wien, 1902.)

(3) F. EXNER and E. HASCHEK: "Wellenlängen Tabellen . . . Bogenspektren." (1904.)

(4) F. EXNER and E. HASCHEK: "Die Spektren der Elemente bei Normalen Druck." I., Hauptlinien der Elemente und Codex der Starken Linien im Bogen und Funken. II., Die Bogenspektren. (Leipzig and Wien, 1911.)

(5) A. HAGENBACH and H. KONEN: "Atlas der Emission Spectra." (Jena, 1905.) English edition by A. S. King. (W. Wesley & Son, London.)

(6) J. M. EDER and E. VALENTA: "Atlas Typischer Spektren." (Wien, 1911.)

(7) H. KAYSER: "Handbuch der Spectroscopie," Vols. V. and VI. (Leipzig, 1910, 1912.) (These include practically all the measures to the dates of publication.)

Many valuable series of measures have since been published in the "Astrophysical Journal" and in the "Zeitschrift für Wissenschaftliche Photographie." The "International Tables of Constants" also include collections of spectroscopic measurements. Collections of tables for the Schumann region are given in Lyman's book.

# CHAPTER II.

## HISTORICAL NOTE.

### 1869—1879.

The earlier attempts to discover laws governing the distribution of lines in spectra were controlled mainly by the supposition that the vibrations which give rise to the lines might be similar to those which occur in the phenomena of sound, and might correspond with harmonical overtones of a single fundamental vibration. In that case the ratios of the wave-lengths of different lines would be expected to be represented by comparatively small integral numbers. Lecoq de Boisbaudran* believed that he had discovered such relations among the bands of nitrogen, but more exact measurements which were made later failed to verify his conclusions. In 1871, however, it was pointed out by Dr. Johnstone Stoney† that the wave-lengths of the first, second, and fourth lines of hydrogen were in the inverse ratio of the numbers 20, 27, and 32, and the accuracy of these ratios strongly suggested the existence of genuine harmonical relations.

The admirable experimental work of Liveing and Dewar,‡ which extended well into the ultra-violet part of the spectrum, provided valuable data for further investigations, and several important features of associated lines were revealed by these observations. In the spectrum of sodium it was observed that successive pairs of lines were alternately sharp and diffuse, and that the pairs generally became fainter and more diffuse as they were more refrangible; at the same time the distance between successive pairs was diminished. (Compare Plate I.) It was remarked that the whole series, excluding the "D" pair, looked very like repetitions of the same set of vibrations in a harmonic progression,§ and it seemed that harmonic relations could be found to subsist between some of the groups. The whole series, however, could not be represented as simple harmonics of one set of six vibrations with any degree of probability. Somewhat similar results were also obtained for potassium, and, later, for the triplets of magnesium.‖

### The Spectrum of Hydrogen.

The discovery by Huggins¶ of a number of prominent lines in the ultra-violet spectra of Sirius and other white stars (Fig. 1), which seemed to be a continuation of the regular series of hydrogen lines in the visible spectrum, led to further search for harmonic ratios in this spectrum on the part of Dr. Johnstone Stoney.** Evidence that the lines in question were all members of the same physical system was found in the fact that when their positions were plotted as abscissæ against ordinates which increased uniformly, they fell upon, or very near, a definite

* Comptes Rendus, **69**, 694 (1869).

† Phil. Mag., **41**, 291 (1871).

‡ Proc. Roy. Soc., **29**, 398 (1879); Collected Papers on Spectroscopy, p. 66.

§ Liveing and Dewar were careful to explain that their reference to harmonic series of lines did not imply that the lines were thought to follow the arithmetical law of an ordinary harmonic progression, but to be comparable with the overtones of a bar or bell.

‖ Proc. Roy. Soc., **32**, 189 (1881).

¶ Phil. Trans., **171**, Pt. II., 669 (1880).

** Quoted by Huggins.

curve. A new departure in the investigation was the substitution of the scale of "wave-frequencies" (the reciprocals of the wave-lengths) for that of wave-lengths. On forming the first and second differences of these wave-numbers, Dr. Stoney concluded (erroneously) that the irregularities in the second differences were too great

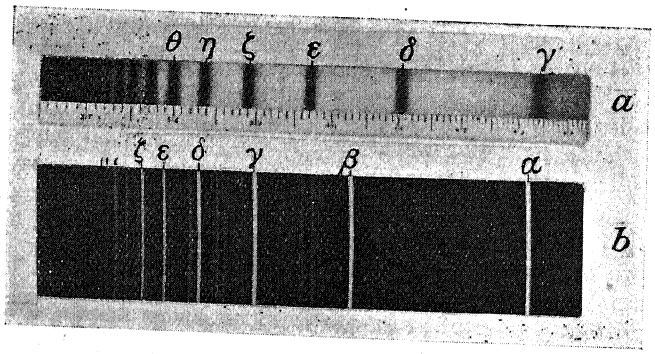


FIG. 1.—THE SPECTRUM OF HYDROGEN: (*a*) IN SIRIUS, (*b*) IN VACUUM TUBE.

to be attributed to errors of measurement, and that the lines did not fall exactly on a smooth curve. Hence it was thought that the lines were not consecutive members of a single series, but members of two or more series, and attention was drawn to several apparently harmonic relations between selected groups of lines.

## SCHUSTER'S CONCLUSIONS.

A discussion of the evidence for the existence of harmonic ratios in spectra was given by Schuster in 1881,* and although it was concluded that the number of such ratios was not greater than might be attributed to chance, Schuster clearly recognised that there might be some undiscovered law, which, in special cases, resolved itself into the law of harmonic ratios. In the light of our present knowledge this is evidently the case for the ratios of the hydrogen lines discovered by Stoney, which follow naturally from the simple law which connects *all* the lines of the series in question; the ratios thus have no special significance, but it is interesting to note that they contain the germ of the true law, and might well have led to its discovery.

That some law existed was sufficiently evident from the distribution of the lines in the hydrogen spectrum, and from the maps of the spectra of sodium and potassium which had been given by Liveing and Dewar, but progress was greatly retarded by the lack of sufficiently exact measurements of the wave-lengths of the lines. Schuster found, for instance, that although all the lines of sodium appeared to be double, and many of those of magnesium triple (compare Plate. II.), the measurements then available showed no regularity in the distances separating the components. Nevertheless, the fact that the hydrogen lines approach each other rapidly as they pass towards the ultra-violet, and that characteristic groups which are repeated several times in other spectra also come nearer and nearer together in the more refrangible parts of the spectrum, was considered by Schuster to furnish a safer basis for further research than the hypothesis of harmonic ratios. It was, in fact, in this direction that subsequent advances were made.

* Proc. Roy. Soc., 31, 337 (1881); Brit. Assoc. Report (1882), p. 120.

### Law of Constant Separations.

A fact of great importance was established by Hartley in 1883,* namely, that the components of doublets or triplets occurring in the same spectrum are of identical separation provided that the positions of the lines are expressed on the scale of oscillation frequencies (or of reciprocal wave-lengths, which are proportional to the frequencies). By the discovery of this law of constant separations, pairs or triplets occurring in different parts of the same spectrum could be associated with certainty.

A further valuable contribution on the experimental side was made by Liveing and Dewar in 1883,† when they gave an account of their work on the ultra-violet spectra of the alkali and alkaline earth metals, and of zinc, thallium, and aluminium, in each of which there are well-marked series. The characteristics which they had previously noted in the case of sodium and magnesium were then found to be equally pronounced in other spectra, and several new series were recorded, including what are now called the principal series of lithium, sodium, and potassium. These observers, however, did not investigate the laws of the series which they described with such completeness and accuracy.

### Balmer's Law for Hydrogen.

A new era commenced in 1885, when the law of the hydrogen series was discovered by Balmer.‡ The number of lines then known to belong to this series, as produced in the laboratory, had been increased to nine by W. H. Vogel,§ and five more had been recorded by Huggins in the spectra of the white stars. Balmer found that the series could be represented, probably within the limits of error of the observations, by a formula of the type

$$\lambda = h\frac{m^2}{m^2-n^2}$$

where $h$ is a constant for the series, and $m$ and $n$ are whole numbers. For the actual lines, using Ångström's measures of the first four lines, he gave the formula

$$\lambda = 3645{\cdot}6\frac{m^2}{m^2-4}$$

where $m$ takes the values, 3, 4, 5, . . . .

Thus

| | Calcd. $\lambda$ | Obsd. $\lambda$ | $O-C$ |
|---|---|---|---|
| $H_\alpha =$ | $\frac{9}{5}h = 6562{\cdot}08$ | 6562·10 | +0·02 |
| $H_\beta =$ | $\frac{4}{3}h = 4860{\cdot}80$ | 4860·74 | −0·06 |
| $H_\gamma =$ | $\frac{25}{21}h = 4340{\cdot}00$ | 4340·10 | +0·10 |
| $H_\delta =$ | $\frac{9}{8}h = 4101{\cdot}30$ | 4101·20 | −0·10 |

* Jour. Chem. Soc., **43**, 390 (1883).
† Phil. Trans., **174**, 187 (1883); Collected Papers, p. 193.
‡ Wied. Ann., **25**, 80 (1885).
§ Monatsb. Königl. Acad., Berlin, July 10 (1879).

The extrapolation to the ultra-violet lines gave values roughly corresponding to the measured wave-lengths, but it remained rather doubtful whether the law was exact or only an approximation to the true formula for the entire series. Subsequent investigations, however, have shown that the law, with a slightly amended constant, represents the whole series with extraordinary accuracy.

Although the hydrogen spectrum is in a sense typical of all series, the simple Balmer formula with modified values of $h$ is not applicable to series in general. Nearly all attempts to represent series of lines by formulæ, however, have been based upon the Balmer law, with the introduction of one or more correcting terms.

Balmer's discovery of the law of the hydrogen series, together with Hartley's law of constant separations and Liveing and Dewar's experimental data, provided a sound basis for further research.

## First Results of Kayser and Runge.

Shortly after the discovery of Balmer's law, the investigation of series spectra was taken up by Kayser and Runge, and by Rydberg. The first results of the former were published in 1888 by Runge,* who announced that formulæ had been found for series of lines of elements other than hydrogen. Their equations were of the form

$$\lambda=\frac{1}{a+bm^{-1}+cm^{-2}} \quad \text{or} \quad \lambda=\frac{1}{a+bm^{-2}+cm^{-4}}$$

where $a$, $b$, $c$ are constants special to each series, and $m$ assumes consecutive values of the series of whole numbers, beginning with 3. The following formula was given for the principal series of lithium, $m$ being 3 for the line $\lambda 3232$ :—

$$\lambda \text{ (in mm.)}=\frac{1}{4341{\cdot}4+136{\cdot}5m^{-1}-11635m^{-2}}$$

It will be observed that the formula is a more general form of that given by Balmer for hydrogen, which may be written

$$\lambda=\frac{hm^2}{m^2-4}=\frac{1}{\frac{1}{h}-\frac{4}{hm^2}}=\frac{1}{a-bm^{-2}}$$

Kayser and Runge were quick to recognise the need for a more accurate knowledge of wave-lengths in such inquiries, and courageously embarked on a new series of determinations with the aid of a large concave grating, beginning with the spectrum of iron as a convenient standard of comparison for purposes of interpolation.†

## The Work of Rydberg.

Rydberg made use of data already to hand, and his investigations are of the utmost importance as having laid the foundation for all subsequent attempts to show the connection between different series occurring in the same spectrum. His first

* Brit. Assoc. Report (1888), p. 576.
† Abhandl. der Berlin Akad. (1890).

memoir was presented to the Swedish Academy of Sciences towards the end of 1889* and gives a comprehensive account of the results at which he had then arrived. As in the case of Kayser and Runge, the ultimate purpose of his inquiries was to gain a more intimate knowledge of the structure of atoms and molecules, and notwithstanding the imperfect data then at his disposal, he discovered most of the important properties of series, and foreshadowed discoveries which were made later, when experimental work provided the necessary data.

Rydberg commenced his work by sorting out doublets and triplets, largely from the tables given by Liveing and Dewar and by Hartley, and in this way ascertained the lines which might properly be associated in the same set of formulæ. Although the terms "doublet" and "triplet" had in general been understood to signify groups of lines not very far apart, Rydberg showed that there were true doublets and triplets in which the components were remote from each other, so that while one component might be in the visible spectrum, another might even be situated in the ultra-violet, other lines occupying the intermediate spaces. Hartley's law of constant separations was thus confirmed and extended, with the proviso that the law was applicable only to members of series of the same species.

Like Johnstone Stoney and Hartley, Rydberg employed the reciprocals of the wave-lengths in place of the oscillation frequencies themselves, but gave them a more definite meaning by defining the "wave-number" as the number of wave-lengths per centimetre; that is, $10^8/\lambda$ in Ångström Units. He pointed out that the use of wave-numbers not only saves a great deal of calculation, but is important in theoretical considerations.

The observation by Liveing and Dewar that pairs or triplets are alternately sharp and diffuse enabled Rydberg to distinguish two species of series, in addition to a third species comprising the ultra-violet lines which the same observers had photographed in the spectra of Li, Na, and K. The first terms of the latter species, which are the most intense in the spectra, are situated in the visible spectrum and had not previously been associated with the ultra-violet series. Three chief species of series were thus recognised as being superposed in the same spectrum, namely :—

*Principal*, including the strongest lines.

*Diffuse*, of intermediate intensity.

*Sharp*, including the weakest lines,

and the members of each series might be single, double, or triple.

In each series the distance from line to line diminishes rapidly on passing to the more refrangible parts of the spectrum, the lines thus converging towards a definite limit, and in a normal series, intensities also diminish in regular order. In a graphical representation with the observed wave-lengths ($\lambda$) or wave-numbers ($\nu$)† of a series as abscissæ, and consecutive whole numbers ($m$) as ordinates, Rydberg found that each series was represented by a regular curve, which appeared to be similar in shape for all series, and to approximate to a rectangular hyperbola (*see*

* Kongl. Svenska Vet.-Akad. Handlingar, Bandet 23, No. 11 (1890) [in French]. Abstracts were given in Comptes Rendus, Feb. (1890); Zeitschr. Phys. Chem., February (1890), and Phil. Mag., April (1890).

† Rydberg represented wave-number by $n$, but analogy with the $\lambda$ always employed for wave-length suggests that $\nu$, as used by Ritz, is more appropriate.

Figs. 2 and 3, pp. 14 and 17). A rough representation of several series was in fact obtained by the use of the hyperbolic formula :—

$$\nu=\nu_\infty-\frac{C}{m+\mu}$$

where $\nu$ is the wave-number of a line, $m$ its order number, and $\nu_\infty$, $C$, and $\mu$ are constants special to each series ; $\nu_\infty$ is the *limit* of the series, being the value of $\nu$ when $m$ is infinite.

Further investigation, however, led to the conclusion that the wave-number should be represented by the equation

$$\nu=\nu_\infty-f(m+\mu)$$

where the form of the function, and any additional constants, would be the same for all series. The simple hyperbolic formula did not fulfil this imposed condition, as the value of $C$ was found to vary very considerably from one series to another. Rydberg then proceeded to investigate the next simplest form of the function, and adopted it in his subsequent work, namely,

$$\nu=\nu_\infty-\frac{N}{(m+\mu)^2}$$

where $N$ is constant for all series.

When $\mu$ is zero this formula becomes identical with that of Balmer for hydrogen, which in terms of wave-numbers, may be written

$$\nu=\nu_\infty\frac{m^2-4}{m^2}=\nu_\infty-\frac{4\nu_\infty}{m^2}=\nu_\infty-\frac{N}{m^2}$$

The constant $N$ could thus be calculated from the hydrogen lines, which gave the value 109,721·6. This, however, was deduced from wave-lengths in air, expressed on the scale of Ångström, and was recalculated later as 109,675·00 from wave-lengths on Rowland's scale, corrected to vacuum.* This number appears in the formulæ for other series, and is generally designated the "Rydberg Constant." Its value on the international scale has recently been given by W. E. Curtis as 109,678·3.

Rydberg fully recognised that the formula which he employed was only an approximation to the true function of $m$ or of $(m+\mu)$, but by its aid he was able to trace a large number of series in the spectra of different elements, and to deduce most of the important properties of series in general.

## Kayser and Runge's Formula.

Almost immediately after the announcement of Rydberg's results, Kayser and Runge published an account of their investigations of the spectra of the alkali metals.† These observers also adopted the scale of wave-numbers per centimetre, and employed the formula

$$\nu=A-\frac{B}{m^2}-\frac{C}{m^4}$$

where $\nu$ is the wave-number, $m$ the order number of a line, and $A$, $B$, $C$ three

* Congrès Internat. de Physique, Paris (1900), p. 211.
† Abhandl. der Berlin Akad. (June 5, 1890).

constants special to each series; $A$ is evidently the limit of the series; $B$ is of the same order of magnitude as Rydberg's constant $N$, but $C$ varies widely from one series to another. The formula was by no means capable of giving an accurate representation of all the lines of a series, and is inferior to that of Rydberg inasmuch as it fails to show the important connection between the Principal and Sharp series. A large number of series and many of the properties of series already described by Rydberg, however, were independently discovered by its use.

Kayser and Runge's formula has passed its period of usefulness, and practically all the newer formulæ represent attempts to improve the original equation of Rydberg. Kayser and Runge, however, made important contributions to the subject by their improved tables of the spectra of many elements,* and by their determinations of the refractive indices of air† which permitted the correction of the wave-numbers to vacuum.

* Abhandl. der Berlin Akad. (1891, 1892, 1893).
† Abhandl. der Berlin Akad. (1893).

# CHAPTER III.

## CHARACTERISTICS OF SERIES.

### General Formula for Hydrogen.

It should be clearly understood that the series spectrum of hydrogen is of exceptional simplicity. The Balmer series, however, does not constitute the whole of the hydrogen spectrum. Another series in the infra-red was predicted by Ritz, and two members at $\lambda$18,751 and $\lambda$12,817·6 have been observed by Paschen. There is also a series in the Schumann region, of which three members have been photographed by Lyman. All the series are included in the general formula

$$\nu = N\left(\frac{1}{m_1^2} - \frac{1}{m^2}\right), \quad m_1 < m$$

where $m_1=1$ for Lyman's series, $=2$ for the Balmer series, and $=3$ for the Ritz-Paschen series. For wave-numbers on the international scale, corrected to vacuum, $N=109{,}678{\cdot}3$ (Curtis).

A graphical representation of these series is given in Fig. 2.

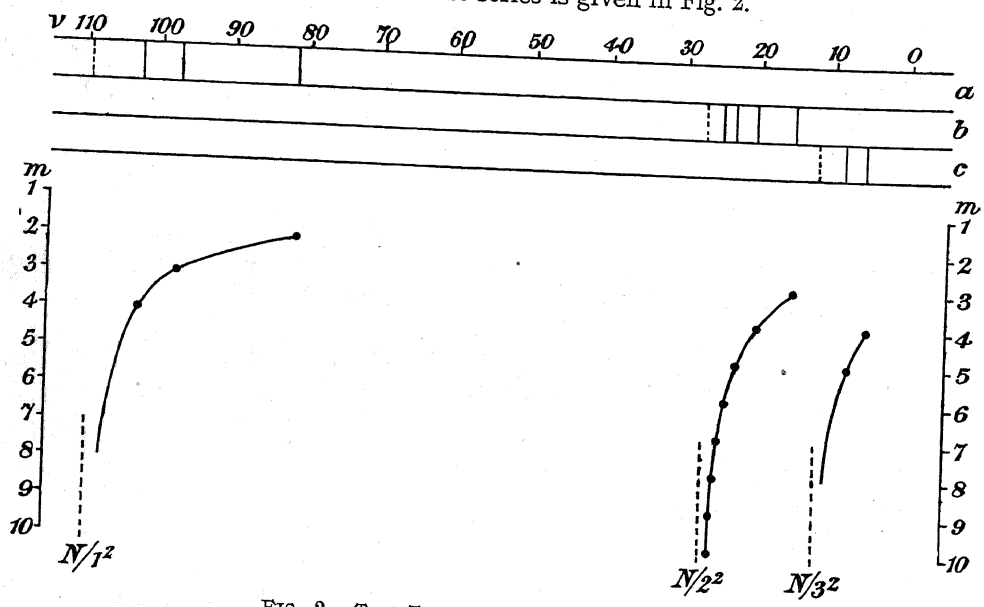


Fig. 2.—The Three Series of Hydrogen.
(a)=Lyman series; (b)=Balmer series; (c)=Ritz-Paschen series.

### The Four Chief Series of Other Elements.

The work of Rydberg, and that of Kayser and Runge, revealed the existence of a large number of series, each of which is generally similar to the Balmer series of hydrogen. In each series the lines become closer, with diminishing intensities, in passing from the red towards the violet end of the spectrum, and converge to a

definite limit (Fig. 3, p. 17). Theoretically, the number of lines in a series is infinite, but no series have actually been traced to their limits. There are no known series in which the lines converge towards the less-refrangible part of the spectrum.

In the general case there are several series superposed in the same spectrum. Several such series are intimately related to each other and may be conveniently regarded as forming a "system" of series. Four of the related series have a certain amount of independence and may be considered to be the chief series of a system. The remainder may be looked upon as derived series.

Three of the chief series were recognised by Rydberg and by Kayser and Runge, namely, in order of intensity :—

Principal, Diffuse, Sharp (Rydberg).
Principal, first Subordinate, second Subordinate (Kayser and Runge).

Rydberg's names are most commonly used and are conveniently abbreviated to $P$, $D$, $S$, while the respective limits may be represented by $P\infty$, $D\infty$, $S\infty$.

The fourth chief series long escaped detection because many of them occur in the infra-red, in which region they were first observed by Bergmann.* They are called "Bergmann series" by some writers, but as they do not all occur in the infra-red, and were not all discovered by Bergmann, the name is not specially appropriate. From theoretical considerations Hicks has named them the "Fundamental" or "F" series, and though they are probably not more fundamental than the other chief series, the name has been so much employed that it will be convenient to retain it for the purposes of the present report.

Although less exact than some of the amended forms which have since been proposed, Rydberg's formula is usually a sufficient approximation to bring out the main characteristics of a system of series, and its simplicity is a great advantage in approaching the subject. This formula will accordingly be adopted for descriptive purposes, namely :—

$$\nu_m = A - \frac{N}{(m+\mu)^2}$$

where $A$ is the limit of the series, $N$ the Rydberg constant for hydrogen, and the wave-numbers $\nu_m$ are obtained by assigning successive integral values to $m$; $\mu$ may be regarded as a decimal part to $m$, though it is sometimes greater than unity. Each series is thus represented by a limit, and a series of "variable parts" or "terms" forming a "sequence."

The four chief series may be represented by the Rydberg formulæ :—

| | | |
|---|---|---|
| Principal... ... ... | $P(m) = P\infty - N/(m+P)^2$ | $m=1, 2, 3 \ldots$ |
| Sharp ... ... ... | $S(m) = S\infty - N/(m+S)^2$ | $m=2, 3, 4 \ldots$ |
| Diffuse ... ... ... | $D(m) = D\infty - N/(m+D)^2$ | $m=2, 3, 4 \ldots$ |
| Fundamental ... ... | $F(m) = F\infty - N/(m+F)^2$ | $m=3, 4, 5 \ldots$ |

where $P(m)$, for example, means the $m$-th line of the $P$ series, and $P$, $S$, $D$, $F$ indicate the values of $\mu$ in the respective series.

These formulæ represent the four chief series of a "singlet" system, but in many systems each member of a series is a doublet or a triplet.

* Dissertation, Jena (1907); Zeit. Wiss. Phot., 6, 113, 145 (1908).

## Relations Between the Chief Series.

The relations between the $P$, $S$, and $D$ series were most completely traced by Rydberg. His method may be usefully illustrated by reference to the spectrum of lithium, which consists of doublets close enough to be regarded as single lines. Rydberg's original formulæ, which are sufficiently accurate for our purpose, were as follows :—

$$P(m)=43{,}487\cdot7-\frac{109{,}721\cdot6}{(m+0\cdot9596)}$$

$$S(m)=28{,}601\cdot1-\frac{109{,}721\cdot6}{(m+0\cdot5951)^2}$$

$$D(m)=28{,}598\cdot5-\frac{109{,}721\cdot6}{(m+0\cdot9974)^2}$$

These formulæ, and similar ones calculated for series of other elements, showed, in the first place, that the limits of the $S$ and $D$ series were probably identical, *i.e.*, $S\infty=D\infty$.

Next, it was found that $m=1$ in the variable part of the formula for $S(m)$ gave approximately the limit of the $P$ series ; thus

$$N/(1\cdot5951)^2=43{,}123\cdot7$$

And, similarly, $m=1$ in the formula for $P(m)$ gave approximately the limit of the $S$ series ; thus

$$N/(1\cdot9596)^2=28{,}573\cdot1$$

From such considerations Rydberg concluded that $P\infty=N/(1+S)^2$ and $S\infty=D\infty=N/(1+P)^2$, so that the three series could be represented by

$$P(m)=\frac{N}{(1+S)^2}-\frac{N}{(m+P)^2}$$

$$S(m)=\frac{N}{(1+P)^2}-\frac{N}{(m+S)^2}$$

$$D(m)=\frac{N}{(1+P)^2}-\frac{N}{(m+D)^2}$$

## The Rydberg-Schuster Law.

The first line of the $P$ series (given by $m=1$) is thus identical with that given by $m=1$ in the $S$ formula, but with opposite sign: *i.e.*, $S(1)=-P(1)$. It follows that *the difference between the limit of the P series and the common limit of the D and S series is equal to the wave-number of the first line of the P series.* This important rule was clearly included in the formulæ given above, but Rydberg did not express it in these terms until 1896,* in which year Schuster† also independently announced its discovery, apparently by reference to the limits of the numerous series which had been calculated by Kayser and Runge. The law of limits is thus generally known as the Rydberg-Schuster law, and is expressed symbolically by

$$P_\infty-S_\infty=P\,(1)$$

* Astrophys. Jour., 4, 91 (August, 1896).
† Nature, 55, 196, 200, 223 (1896).

### Runge's Law.

Runge* was the first to point out that the difference between the limits of the $D$ and $F$ series is equal to the wave-number of the first $D$ line (mostly given by $m=2$ in Rydberg's formulæ). This relation is often referred to as Runge's law, and is expressed symbolically by

$$D_\infty - F_\infty = D\ (2)$$

Thus, in Rydberg's form,

$$F_\infty = N/(2+D)^2\ ; \quad \text{and } F(m) = N/(2+D)^2 - N/(m+F)^2.$$

In all series of this type the value of $F$ approximates to unity.

### Abbreviated Notation.

A convenient and now indispensable abbreviated notation for series was suggested by Ritz in connection with the more complex formula which he employed. It is, however, of general application, and merely provides that a term $N/(m+\mu)^2$ or its

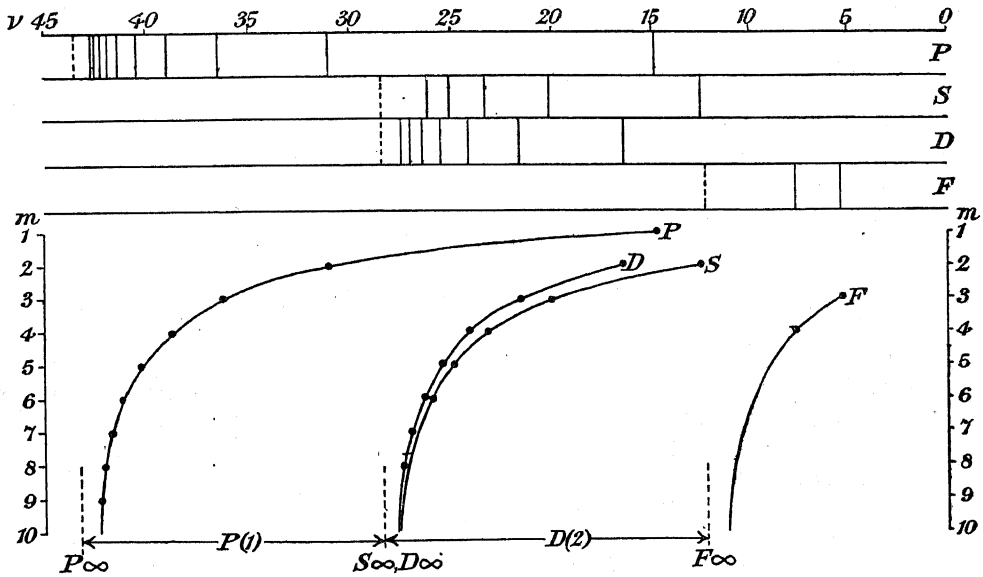


Fig. 3.—The Four Chief Series of Lithium.

equivalent should be represented by $m\mu$, or by $mP$, $mS$, $mD$, $mF$ in relation to individual series. Thus the four chief series are written

$$\begin{aligned} P(m) &= 1S - mP \\ S(m) &= 1P - mS \\ D(m) &= 1P - mD \\ F(m) &= 2D - mF \end{aligned}$$

It is to be understood that while $D(3)$, for example, indicates the *line* in the $D$ series for which $m=3$, $3D$ is equivalent to the *term* $N/(3+D)^2$ and represents the interval from the line $D(3)$ to $D_\infty$.

* Phys. Zeit., 9, 1 (1908).

The foregoing relations, in the case of lithium, are represented graphically in Fig. 3, p. 17.

In order to distinguish series of different kinds, Paschen designated singlet systems by the use of capital letters, and doublets and triplets by small letters. Following a suggestion made by Prof. Saunders, however, it will be convenient to adopt Greek letters for doublets, and small letters for triplets. Thus

$P,\ S,\ D,\ F$ = Singlet systems.
$\pi,\ \sigma,\ \delta,\ \varphi$ = Doublet ,,
$p,\ s,\ d,\ f$ = Triplet ,,

For general descriptive purposes, however, we shall occasionally use $P, S, D, F$ for any class of series.

### Doublet Systems.

The special characteristics of a doublet system, such as that of sodium (*see* Plate I.), assuming that there are no complications due to satellites, may be briefly stated as follows:

(1) In the $\delta$ and $\sigma$ series, the less refrangible components of the pairs are the stronger, and the separations of the components, when expressed in wave-numbers, are constant throughout.

(2) In the $\pi$ series, the more refrangible components of the pairs are the stronger, and the *first* pair has the same separation as $\delta$ and $\sigma$. The components approach each other as the order number increases, and the two series have the same limit.

(3) The $\varphi$ series consists of single lines.

These characteristics are embodied in the following formulæ, where the brighter components are indicated by $\pi_1$, $\sigma_1$, $\delta_1$, and the fainter by $\pi_2$, $\sigma_2$, $\delta_2$:—

| Rydberg formulæ. | Abbreviations. | |
|---|---|---|
| $\pi_1(m)=N/(1+\sigma)^2-N/(m+\pi_1)^2$ | $=1\sigma-m\pi_1$ | Shorter $\lambda$ |
| $\pi_2(m)=N/(1+\sigma)^2-N/(m+\pi_2)^2$ | $=1\sigma-m\pi_2$ | Longer $\lambda$ |
| $\sigma_1(m)=N/(1+\pi_1)^2-N/(m+\sigma)^2$ | $=1\pi_1-m\sigma$ | Longer $\lambda$ |
| $\sigma_2(m)=N/(1+\pi_2)^2-N/(m+\sigma)^2$ | $=1\pi_2-m\sigma$ | Shorter $\lambda$ |
| $\delta_1(m)=N/(1+\pi_1)^2-N/(m+\delta)^2$ | $=1\pi_1-m\delta$ | Longer $\lambda$ |
| $\delta_2(m)=N/(1+\pi_2)^2-N/(m+\delta)^2$ | $=1\pi_2-m\delta$ | Shorter $\lambda$ |
| $\varphi(m)=N/(2+\delta)^2-N/(m+\varphi)^2$ | $=2\delta-m\varphi$ | |

There is sufficient reason to believe that the relations implied by these formulæ are exact, notwithstanding that the lines composing a series are only imperfectly represented by the simple Rydberg formula. The doublet separation is evidently given by $1\pi_2-1\pi_1$.

Ritz suggested that the variable part of the formula for the fundamental series might be represented by $m\Delta\pi$, where $\Delta\pi=\pi_2-\pi_1$; or, more fully,

$$m\Delta\pi=N/[m+(\pi_2-\pi_1)]^2$$

The relation, however, is not exact and the fundamental series is now regarded as one of the four chief series of a system, having a certain degree of independence. Ritz's form is approximately correct because $\pi_2-\pi_1$ is mostly small, so that $m+(\pi_2-\pi_1)$ is nearly an integer.

### Triplet Systems.

The characteristics of a triplet system, such as that of magnesium, in which there are no satellites, may be summarised as follows :

(1) In the $d$ and $s$ series the least refrangible component is ordinarily the strongest line and the most refrangible the weakest. The wave-number separations are constant for all members of the $d$ and $s$ series, and the wider separation is that of the two less refrangible members. The wider separation is usually rather more than double the narrower.

(2) In the $p$ series, the order of intensities is inverted and the wider separation is on the more refrangible side (usually excepting the first triplet). The series formed of corresponding lines converge to the same limit.

(3) The $f$ series consists of single lines.

Thus, in the abbreviated notation, the four chief series in a system of triplets without satellites are written in the form

$$\left.\begin{array}{ll} p_1(m)=1s-mp_1 & \text{Shorter } \lambda \\ p_2(m)=1s-mp_2 & \\ p_3(m)=1s-mp_3 & \text{Longer } \lambda \end{array}\right\} \text{ or } p_i(m)=1s-mp_i$$

$$\left.\begin{array}{ll} s_1(m)=1p_1-ms & \text{Longer } \lambda \\ s_2(m)=1p_2-ms & \\ s_3(m)=1p_3-ms & \text{Shorter } \lambda \end{array}\right\} \text{ or } s_i(m)=1p_i-ms$$

$$\left.\begin{array}{ll} d_1(m)=1p_1-md & \text{Longer } \lambda \\ d_2(m)=1p_2-md & \\ d_3(m)=1p_3-md & \text{Shorter } \lambda \end{array}\right\} \text{ or } d_i(m)=1p_i-md \quad i=1, 2, 3$$

$$f(m)=2d-mf$$

A triplet system, as will appear from the tables, is nearly always accompanied by a system of singlets. Combination lines arising from the two systems are found, and it is possible that the singlets form an essential feature of a fully observed triplet system.

### Satellites.

In many spectra the series are rendered more complicated by the presence of *satellites* which accompany some of the chief lines. Evidence of the existence of satellites was found by Rydberg, who regarded them as secondary diffuse series, but their true nature was not revealed until Kayser and Runge made their more exact observations of spectra.

These satellites are found in connection with doublets and triplets of the diffuse series. In doublet series, it is the less refrangible line of each diffuse pair which has a fainter companion or satellite, and the satellite is ordinarily on the side towards the red. The brighter component, $\delta_1$, is then displaced from its normal position, and it is the satellite which follows the law of constant separation. The chief line approaches the satellite as the order number increases, and the common limit is identical with that of the normal members of the $\sigma_1$ series.

In a doublet system which includes satellites, the formulæ for the principal and sharp series are unmodified, but the $\delta$ formulæ become

$\delta_1'(m)=1\pi_1-m\delta'$ (satellite).
$\delta_1(m)=1\pi_1-m\delta$ (first chief line, longer $\lambda$).
$\delta_2(m)=1\pi_2-m\delta'$ (second chief line, shorter $\lambda$).

It will be observed that there will now be two limits for the fundamental series, given by $2\delta$ and $2\delta'$, and consequently the members of this series will be doublets, with a constant separation equal to the separation of the satellite and chief line in the first $\delta$ pair (usually given, it must be remembered, by $m=2$). That is

$$\begin{cases} \varphi_1(m)=2\delta-m\varphi & \text{Brighter, less refrangible component.} \\ \varphi_2(m)=2\delta'-m\varphi & \text{Fainter, more refrangible component.} \end{cases}$$

These relations are shown diagrammatically in Fig. 4*a*. An example of a $\delta$ pair with satellite appears in the spark spectrum of barium, Plate IV.

In a triplet system, the least refrangible components of the diffuse triplets have two satellites, the middle lines one, and the most refrangible components no satellite at all. The outer satellite to the first line is the faintest of the group (Fig. 4*b*). It is the satellite to the middle line, and the outer satellite of the least refrangible component which usually show the normal triplet separation given by the sharp series, and the separation of the satellite from the middle line is identical with that of the two satellites to the first chief line. (*See also* Pl. III*c*.)

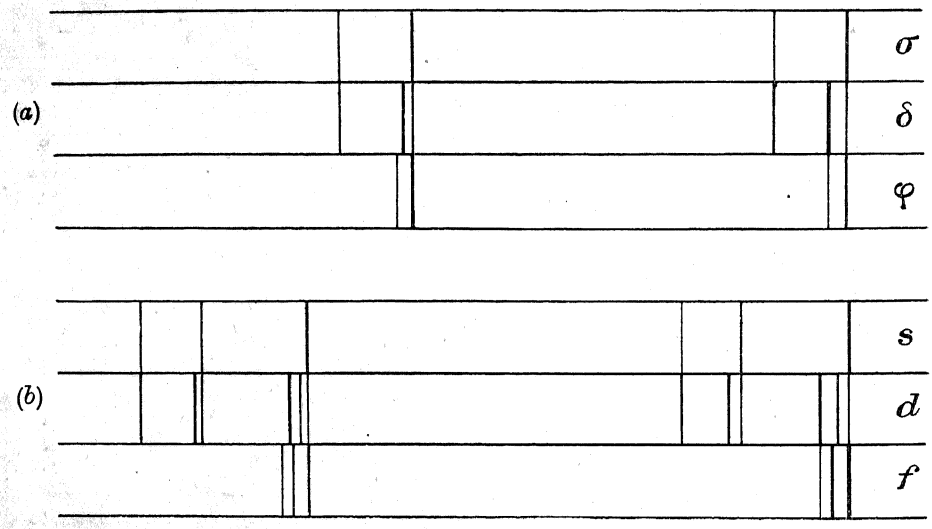


FIG. 4.—DIAGRAM ILLUSTRATING ARRANGEMENT OF SATELLITES—(*a*) IN DOUBLET SERIES; (*b*) IN TRIPLET SERIES.

With increase of order number the displacements of the chief lines diminish, and ultimately vanish. There are thus six series in the *d* group when satellites are present, but there are only three limits, which are identical with the three limits of the *s* series.

The formulæ for the diffuse series of triplets thus require the following extensions:

| | | Index numbers. |
|---|---|---|
| $d_1''(m)=1p_1-md''$ | Satellites | 13 |
| $d_1'(m)=1p_1-md'$ | Satellites | 12 |
| $d_1(m)=1p_1-md$ | First chief line, longer $\lambda$ | 11 |
| $d_2''(m)=1p_2-md''$ | Satellite | 23 |
| $d_2(m)=1p_2-md'$ | Second chief line | 22 |
| $d_3(m)=1p_3-md''$ | Third chief line, shorter $\lambda$ | 33 |

The index numbers suggested by Rydberg, and still sometimes used, are shown on the right. $d(4)_{13}$, for example, would indicate the outer satellite of the first component of the triplet for which $m=4$ in the formula representing the series.

There are now three values of the term $2d$, and therefore three limits for the fundamental series. The fundamental series accordingly consists of narrower triplets in which the separations of the components are constant and equal to those of the first chief line and its two satellites in the first member of the $d$ series. Symbolically we have—

$f_1(m)=2d-mf$ Brightest, least refrangible, component.
$f_2(m)=2d'-mf$
$f_3(m)=2d''-mf$ Faintest, most refrangible, component.

As shown in Fig. 4*b*, the brightest component and the wider separation are towards the red, as in the $s$ and $d$ triplets.

It is quite possible that satellites are a normal feature of the diffuse series of doublets and triplets, and that their apparent absence in some cases may be due to their small separations from the chief lines.

The probable existence of satellites in some of the fundamental series was first suggested by Hicks. In the case of the triplets of strontium and barium they have since been fully established by Saunders from photographs of the arc in vacuo (*see* tables for these elements). The structure of a fundamental triplet having satellites appears to be identical with that of a diffuse triplet, the first line having two satellites and the second line one. Additional terms $mf'$ and $mf''$ thus make their appearance, and the triplet is represented symbolically in the following way:

$$f_1(m)=\begin{cases}2d-mf''\\2d-mf'\\2d-mf\end{cases}\qquad f_2(m)=\begin{cases}2d'-mf''\\2d'-mf'\end{cases}\qquad f_3(m)=2d''-mf''$$

The photograph reproduced in Plate III.(*b*) shows the details of a fundamental triplet of barium. It is from a negative by A. S. King,* the source of light being an electric furnace containing barium vapour at a low pressure.

## Negative Wave-numbers.

It has already been explained that the first member of the $S$ series is identical with the first of $P$, but is of opposite sign in the respective formulæ. In the doublets of the alkali metals, the pair which is common to the two series appears with positive sign in $P$ and with negative sign in $S$. In the doublets of some elements, however, as in aluminium, the first pair has a positive sign in $S$, and a negative sign in $P$. The first $P$ pair then appears to be out of step with the other $P$ lines, and the stronger component is on the *less* refrangible side; also the limit of the $P$ series is on the red side of the common limit of $D$ and $S$, whereas in the alkali doublets it is on the violet side.

It tends to clearness of thought in all such considerations to construct diagrams, as in Fig. 5, showing the negative as well as the positive scale of wave-numbers, and, when the series have been plotted, to imagine the negative members to be folded back into the positive part of the spectrum. This will ensure a proper conception of the appearance which any negative group will present in the actual spectrum.

* Astrophys. Jour., **48**, Plate III (1918).

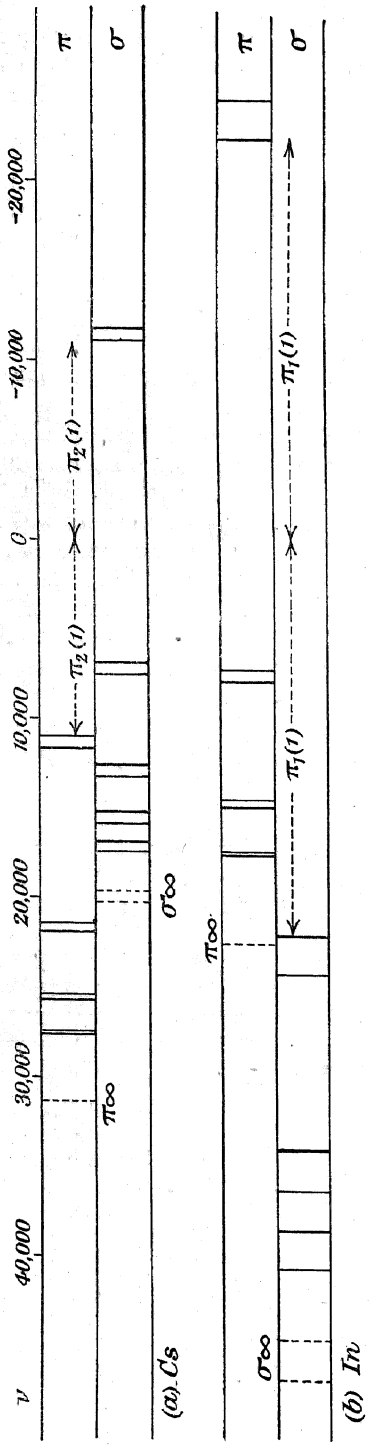


FIG. 5.—(*a*) SERIES IN WHICH $P(1)$ IS POSITIVE; (*b*) SERIES IN WHICH $P(1)$ IS NEGATIVE.

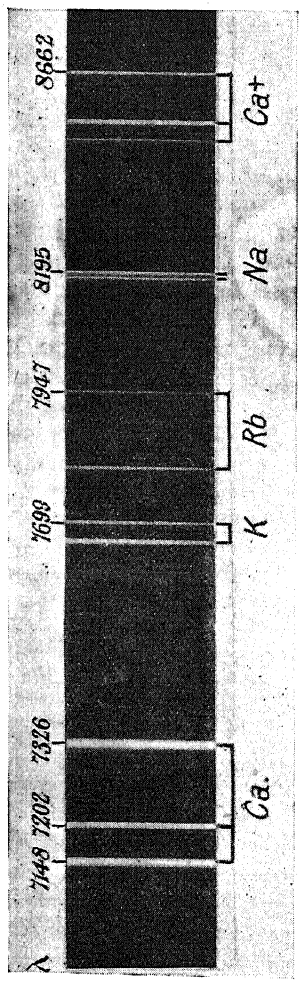


FIG. 6.—PHOTOGRAPH SHOWING AN INVERTED DIFFUSE DOUBLET OF IONISED CALCIUM. (λλ 8662, 8542, 8498)

A diffuse pair of Na (8195, 8184), the first principal pair of Rb (7947, 7800), and the first principal pair of K (7699, 7665) appear as impurities. (Photograph by Col. E. H. Grove-Hills, R.E., 1895.)

Doublet series with positive and negative $P(1)$ are thus illustrated in Fig. 5.

When $P(1)$ occurs with negative sign in a triplet series, as is usually the case, the first triplet is inverted, the brightest component and the wider separation being then on the less refrangible side, as in the triplets of the sharp and diffuse series. In the remaining triplets, however, the stronger component and wider separation are on the more refrangible side.

The first member of the diffuse series also sometimes appears with negative sign, and the corresponding doublet or triplet is then reversed right and left in the actual spectrum. An interesting example appears in Fig. 6, where the lines 8662, 8542, 8498 of ionised calcium (*see* p. 25) form an inverted diffuse doublet with satellite.

In the tables which accompany this report negative members are indicated by the usual minus sign. The occurrence of these negative signs is probably of no great theoretical importance, because the "terms" from which the lines are derived by taking differences are always positive.

## The Combination Principle.

The possible existence of other series which would be related to the chief series already considered was first suggested by Rydberg,* who pointed out that in his general formula

$$\frac{\nu}{N}=\frac{1}{(m_1+\mu_1)^2}-\frac{1}{(m_2+\mu_2)^2}$$

where $m_1$ was usually $=1$, it might be supposed very probable that $m_1$ as well as $m_2$ would be variable. Such variation of $m_1$ would evidently give rise to other series running parallel to the first. Rydberg was unable to establish any such series, but the idea was developed later by Ritz.†

The lines of a series always appear as the difference of two terms, one of which is the limit of the series, and the other a "variable part" or "term" of a sequence given by successive integral values of $m$; the limit itself in the case of the chief series is the first term of the sequence of one of the other series. Ritz discovered that lines which were computed by taking differences of other terms of the four chief sequences were often found in the actual spectra, and he called them "combination lines," or "combination series" when more than one line was derived from the same sequence. Thus, there might be series $2\,S-mP$, $3\,S-mP$, as well as the chief series, $1\,S-mP$; or $1\,S-mD$, $1\,P-mP$, and so on. The fundamental, or "Bergmann," series was at first regarded by Ritz as the combination series, $2D-m\Delta P$, as already explained on p. 18, but is now to be considered as one of the chief series.

The extensive investigations of infra-red spectra subsequently made by Paschen and his pupils have revealed a very large number of combination lines, and have shown that the combination principle is probably exact. The application of this principle has shown that many lines which previously appeared to be unattached really form part of regular systems, of which the principal, sharp, diffuse and fundamental series are the chief members, and it seems possible that in spectra in which series have not yet been identified the complexity may be due to the existence of a great number of combinations.

It is interesting to observe that the proof of the combination principle is independent of a knowledge of the true series formula, or even of the exact limits of the various

* Loc. cit., p. 73.

† Phys. Zeit., **9**, 521 (1908); Astrophys. Jour., **28**, 237 (1908).

series. The limits can, in fact, be determined with considerable accuracy in most cases; but by assuming the Rydberg and Runge laws to be exact, and adopting a limit for one of the series, all the limits will be equally in error. Then, if the variable terms *mp*, *ms*, &c., be derived by subtracting the observed wave-numbers of the lines from the adopted limits of their respective series, these terms will be equally affected by any error in the limit first adopted. Hence, the errors will cancel each other in taking differences to form the various combinations. An example may be taken from lithium (*see* table for this element) by way of illustration. The limit calculated for the principal series is 43,486·3, and $\pi$ (1) is 14,903·8; thus

$$\begin{array}{rll} \pi_\infty & =43{,}486{\cdot}3=1\ \sigma & \text{(calculated from actual lines)} \\ \pi(1) & =14{,}903{\cdot}8 & \text{(observed first principal line)} \\ \therefore\ \sigma_\infty & =\delta_\infty=28{,}582{\cdot}5=1\ \pi & \text{(Rydberg-Schuster law)} \\ \delta(2) & =16{,}379{\cdot}4 & \text{(observed first diffuse line)} \\ \therefore\ \varphi_\infty & =12{,}203{\cdot}1=2\ \delta & \text{(Runge's law)} \end{array}$$

Thus, starting with $\pi_\infty$, the limits of the other chief series are obtained without independent calculation from the lines themselves. The "terms" $m\pi$, $m\sigma$, $m\delta$, $m\varphi$ may then be calculated by subtracting the observed wave-numbers from the limits of the respective series, and such a combination as $2\sigma-2\pi$ may then be formed as follows:—

$$\begin{array}{rl} \sigma_\infty & =28{,}582{\cdot}5 \\ \sigma(2) & =12{,}302{\cdot}0 \\ \hline 2\sigma & =16{,}280{\cdot}5 \end{array} \qquad \begin{array}{rl} \pi_\infty & =43{,}486{\cdot}3 \\ \pi(2) & =30{,}925{\cdot}9 \\ \hline 2\pi & =12{,}560{\cdot}4 \end{array}$$

$$2\sigma-2\pi=3{,}720{\cdot}1 \text{ calculated}$$
$$3{,}719{\cdot}9 \text{ observed}$$

If the calculation be repeated with any other value of $\pi_\infty$, the final result for the combination will be unchanged. This not only verifies the general validity of the combination principle, but also indicates the truth of the Rydberg-Schuster and Runge laws, since such calculations are based on the assumption that these laws are true. An exact series formula would doubtless conform with all these relations, but the above procedure renders the calculated combinations independent of a knowledge of the true series formula. Including the satellite terms, the possible combinations are very numerous, as will appear from many of the tables for individual elements.

## Enhanced Line Series.

It has been shown by Fowler* that the enhanced lines of helium, magnesium, calcium and strontium form families of series identical in their mutual relationships with those formed by arc lines. The enhanced series, however, differ from the ordinary series in the important particular that the series constant takes four times its normal value, so that the approximate formula for such a series would be

$$\nu_E=A-4N/(m+\mu)^2$$

Hicks has since identified the corresponding series in barium, and other unpublished examples have been found by the author.

* Phil. Trans., A, **214**, 225 (1914).

This feature is obviously of importance in connection with theories of spectra. On Bohr's theory, while the ordinary series lines are emitted during the re-formation of atoms from which one electron has been displaced, the enhanced lines are generated when *one* electron returns to an atom from which two electrons have been detached. The multiple 4 thus appears as the square of 2 in the theoretical formula for enhanced series.

Adopting this interpretation, it has been proposed by Saunders and others that series of enhanced lines should be referred to as series belonging to *ionised* elements—*e.g.*, ionised helium, &c. The adopted symbol for an ionised element is $He^+$, $Ca^+$, &c.

## Identification of Series.

In seeking to arrange lines in series, it is necessary to bear in mind at the outset that lines belonging to the same series have usually the same physical characteristics, and diminish regularly in intensity in passing to the shorter wave-lengths. Thus, it frequently happens that lines which form a series can be picked out by inspection of photographs of the spectra, or of maps constructed from tables in such a way as to show the relative intensities of the lines. General confirmation may usually be found by drawing a graph with the lines themselves as abscissæ, and successive integers as ordinates, when regularity of the curve would be a strong indication that the lines had been properly allocated. A further test might then be made by the calculation of a formula, or by reference to Rydberg's table (Chapter IV.).

In the case of doublets and triplets, one would naturally first sort out pairs or triplets of constant wave-number separation, and then try to arrange them in a series system.

One of the most valuable tests of the proper allocation of lines in doubtful cases, and especially when only a few lines have been observed, is provided by the behaviour of the lines in a magnetic field ; that is, by " Zeeman effects." Preston* was the first to observe that all lines belonging to the same series showed identical magnetic resolutions, not only in type of resolution, but also in wave-number separation of the components. Corresponding series in the spectra of several groups of elements were also found to behave in the same way.

When the source is viewed at right angles to the direction of the magnetic field, the helium lines all show the " normal triplet " appearance. In the case of the sodium lines, $D_1$ exhibits four components and $D_2$ six, and exactly similar resolutions are shown by corresponding pairs of the other elements which appear in the same group of the periodic table—namely, K, Rb, Cs, Cu, Ag and Au. Further, the same types of resolutions were found by Runge and Paschen for certain pairs in Mg, Ca, Sr, Br and Ra,† and the inference that these belonged to principal series has since been fully confirmed by the observation of other members of the series in the region of short wave-lengths and their connection in series of enhanced lines. Pairs of the sharp series show similar resolutions, but in inverse order, in accordance with the Rydberg relationship of the sharp and principal series.

Characteristic resolutions have also been observed in the principal and sharp triplet series. For the diffuse triplets the resolutions are less simply related, being the same for lines of the same series, but varying in corresponding series of different elements.

* Trans. Roy. Soc. Dublin (2), **7**, 7 (1899).
† Astrophys. Jour., **16**, 123 (1902); **17**, 232 (1903).

A valuable summary of such observations has been given by Zeeman in his book on "Magneto-Optics."*

### Spectra with Constant Differences.

In the spectra of many elements in which series of the regular types have not been identified, there are pairs or groups of lines with constant wave-number separations which occur several times. This type of regularity was first noted by Kayser† in the spectra of tin, lead, arsenic, antimony, bismuth, palladium, platinum and ruthenium. Other examples were found by Rydberg‡ in the red spectrum of argon and in the spectrum of copper. The spectra of about 40 elements have since been investigated from this point of view by Emil Paulson.§ Examples of such constant difference are given in the general tables.

The question naturally arises as to whether this kind of spectrum structure represents a second type of regularity, as originally suggested by Kayser, or has its origin in a multitude of combination terms. The recent remarkable work of Meissner and Paschen on the spectrum of Neon (*see* Neon) is highly suggestive in this connection. In this spectrum a large number of constant difference groups had been identified, but it has now been found that the lines may be arranged in about 132 series, which are closely inter-related. Several of the series run parallel to each other, and thus give rise to pairs or groups with constant differences. The individual series are mostly quite normal, but the spectrum differs from those previously described in having several series of each type. It would seem possible that other constant-difference spectra may be built up in a similar manner.

It is of importance to note that there are spectra which are intermediate between the constant-difference spectra and those which show series of the more usual types. Thus, in calcium and strontium (*see* tables) there are constant-difference triplets which have the *same* separations as those falling in the regular series, and pairs having separations equal to one or other of the triplet intervals. In copper, on the other hand, the constant-difference pairs and triplets found by Rydberg have no obvious relation to the separations of the pairs which constitute the regular series.

Macmillan & Co., Ltd. (1913), pp. 65 and 162.

† Handbuch, **2**, 573; Abh., Berlin Akad. (1893, 1897).

‡ Astrophys. Jour., **6**, 239, 338 (1897).

§ Beiträge zur Kenntnis der Linienspektren. Dissn. Lund (1914). Astrophys. Jour., **40**, 298 (1914); **41**, 72 (1915), Y, A. Phil. Mag., **29**, 154 (1915), Pd. Ann. d. Phys., **45**, 1203 (1914), La; **46**, 698 (1915), Pt. Phys. Zeit., **15**, 892 (1914), Sc.; **16**, 7 (1915), Gd; **16**, 81, Ru; **16**, 352, Ru, Nb, Tm; **19**, 13 (1918), Ni. Zeit. Wiss. Phot., **18**, 202 (1919), Pd, Y.

# CHAPTER IV.

## RYDBERG'S FORMULA.

### THE RYDBERG CONSTANT.

As already pointed out, the Rydberg series constant is derived from the lines of hydrogen, for which the Balmer formula gives

$$N=\frac{4m^2}{m^2-4}\cdot\nu$$

The wave-lengths of the first six lines as determined on the international scale by W. E. Curtis * are probably the most accurate at present available for the calculation of $N$. The details are as follows :—

| Line. | $m$. | λ I. A. | Prob. error. | λ Vac. | Vac. | $N$. |
|---|---|---|---|---|---|---|
| α | 3 | 6562·793 | ±0·0017 | 6564·6022 | 15233·216 | 109679·155 |
| β | 4 | 4861·326 | 0·0010 | 4862·6797 | 20564·793 | 8·896 |
| γ | 5 | 4340·467 | 0·0006 | 4341·6830 | 23032·543 | 8·776 |
| δ | 6 | 4101·738 | 0·0013 | 4102·8915 | 24373·055 | 8·748 |
| ε | 7 | 3970·075 | 0·0016 | 3971·1940 | 25181·343 | 8·738 |
| ζ | 8 | 3889·051 | ±0·0011 | 3890·1489 | 25705·957 | 8·750 |

It will be observed that there is a small systematic variation in the values of $N$ yielded by successive lines, the value diminishing as the order number increases, indicating a slight departure from Balmer's law. The question is complicated, however, by the fact that the lines are very close doublets ($\Delta\lambda$ in $H_\alpha=0{\cdot}145\ A$, and in $H_\beta=0{\cdot}093A$)†, in which the less refrangible components are the stronger. Curtis's measures refer to the " optical centres of gravity " of these pairs, and it is clear that the simple Balmer formula does not strictly hold for these points. It is further probable that neither of the components is exactly represented by the Balmer formula.

From an application of the general Rydberg formula, Curtis concludes that the most probable value of $N$, as determined from the hydrogen lines, is 109,678·3, for wave-numbers on the international scale, corrected to vacuum.

Determinations of the value of $N$ from any other series are at present of little weight, as the true form of the series equation remains unknown. As an indication of the approximate constancy of $N$ for most series, however, the following values calculated by Paulson‡ by the use of the Ritz formula, to be mentioned later, may be quoted :

| | |
|---|---|
| Lithium | $N=109347{\cdot}5$ |
| Sodium | $N=109358{\cdot}5$ |
| Potassium | $N=110404{\cdot}5$ |
| Rubidium | $N=110087{\cdot}0$ |
| Helium | $N=109657{\cdot}2$ |

These values are clearly not inconsistent with a constant $N$, since the formulæ employed were only approximate.

* Proc. Roy. Soc., A, **90**, 605 (1914) ; A, **96**, 147 (1919).
† Merton, Proc. Roy. Soc., A, **97**, 307 (1920).
‡ Kongl. Fysiog. Sällskapets Handl., N.F. Bd. 25, No. 12, p. 12.

It should be noted, however, that Bohr's theory of spectra demands a small variation of $N$ depending upon the atomic weight of the element. (*See* Chapter IX.)

### THE CONSTANTS $\mu$ AND $A$.

Rydberg pointed out that the most natural method of calculating the constants in his formulæ would be to apply the method of least squares, but he did not consider the data then available to be sufficiently accurate to justify the labour involved. The equation being of the third degree, the least square method is not directly applicable, and it would be necessary first to find approximate values which could be corrected by the more exact method. In fact, it is necessary, or at least useful, to find a set of preliminary values of the constants of the Rydberg formula whatever series equation be adopted.

If two consecutive terms of a series be denoted by $\nu_m$ and $\nu_{m+1}$,

$$\nu_m = A - \frac{N}{(m+\mu)^2}$$

$$\nu_{m+1} = A - \frac{N}{(m+1+\mu)^2}$$

and

$$\nu_{m+1} - \nu_m = \frac{N}{(m+\mu)^2} - \frac{N}{(m+1+\mu)^2}$$

The value of $(m+\mu)$, and thence of $A$, can thus be determined by successive approximations, $N$ being taken as 109678·3.

*Rydberg's Interpolation Table.*—It is more convenient, however, to determine the approximate values of the constants $\mu$ and $A$ with the aid of an interpolation table such as was constructed by Rydberg, and then to correct them. This table gives values of the function $N/(m+\mu)^2$ or of $(A-\nu)$, corresponding to values of $(m+\mu)$, ranging from 1·00 to 10·00, together with the differences between consecutive values of the function as $m$ is varied. Rydberg's table was computed with $N=109721·6$, and is still useful, but for the present report new computations to the nearest unit in wave-numbers have been made with Curtis's value of $N$—namely, 109678·3. The revised functions are given in Table III.

The table will at once give a useful indication as to whether lines suspected of forming a series really do so. Thus, if the interval between two successive lines is 9,057, the table shows that the next line in a normal series would follow after an interval of about 3,676, and the following one after another interval of about 1,846. These would be the intervals if Rydberg's formula were exact, and in practice are only to be taken as indicating the order of magnitude of successive steps from line to line.

But although Rydberg's formula is not exact, the table is almost indispensable in the preliminary calculation of constants when other more accurate formulæ are used. As an example of its use, let two consecutive lines of a series be $\nu$16,226 and $\nu$19,398. The interval between the lines is 3,172, and from the table we find

$$\Delta\nu\ 3{,}184 = \frac{N}{(3·64)^2} - \frac{N}{(4·64)^2} = 8{,}278 - 5{,}094$$

$$\Delta\nu\ 3{,}161 = \frac{N}{(3·65)^2} - \frac{N}{(4·65)^2} = 8{,}233 - 5{,}072$$

Interpolation readily gives

$$\Delta\nu\ 3{,}172=\frac{N}{(3{\cdot}645)^2}-\frac{N}{(4{\cdot}645)^2}=8{,}255-5{,}083$$

Then

$$\left.\begin{aligned}A&=16{,}226+8{,}255=24{,}481\\ \text{or,}\quad A&=19{,}398+5{,}083=24{,}481\end{aligned}\right\}$$

The approximate equation for the series, therefore, is

$$\nu=24{,}481-\frac{N}{(m+0{\cdot}645)^2}$$

Succeeding members of the series would then be obtained by putting $m=5$, 6, &c., the second terms again being obtained from the table.

As the Rydberg formula does not usually represent a series with an accuracy equal to that of the observations, different pairs of lines may lead to slightly different values of $\mu$ and $A$. In order to distribute the errors, and so get a more even representation of the whole series, Rydberg's procedure was to weight the lines in proportion to the squares of the wave-lengths. It is no longer necessary to do this, as when more than two members of a series are available a more exact formula may be used, such as that of Ritz or Hicks.

## The Order Numbers of the Lines.

The numeration of the lines when Rydberg's formula is used is by no means a matter of indifference. The numbers actually found by the formula, or from the table, are values of $(m+\mu)$, so that $m$ and $\mu$ are not separately determined. To obtain definitive values of $m$ in a system of series Rydberg made use of the relations which he had discovered between the $P$ and $S$ series. Thus the yellow lines of sodium, having the same separation as the pairs of the $D$ and $S$ series, must be $P(1)$, and the order numbers in the $P$ series must be assigned accordingly. The numeration of the lines in $S$ must also be such that $m=1$ in its formula gives a result corresponding approximately with $-P(1)$. The latter criterion is also applicable to singlet series when the first $P$ line occurs in the region covered by the observations. Thus, in the $P$ series of Na, K, Cs, Rb, if $m=1$ is to give the first member, $\mu$ must be $>1$; and in the associated $S$ series $m=1$ will then give $P(1)$ with negative sign, with $\mu<1$; in such systems $P_\infty$ is $> S_\infty$. In many cases, however, as in the triplet series of Mg, Ca, Sr, and in the doublets of Al, $P < S_\infty$ (*i.e.*, the $P$ series lies on the less refrangible side of $D$ and $S$), and $\mu$ must then be $>1$ in the formulæ for $S$ in order that $m=1$ may give the first $P$; $S(1)$ then appears with positive sign, and $P(1)$ has a negative sign as given by $m=1$ in the formula for the $P$ series.

The assignment of the order numbers in the $D$ series remains somewhat arbitrary. Since $D$ and $S$ converge to the same limit, the members of the two series come closer together as the limit is approached, and it would seem most natural to give neighbouring lines the same number in the two series, especially in such cases as potassium, where $D$ and $S$ pairs are nearly coincident in position. In most series the first observed $D$ is given by $m=2$ when this procedure is adopted, and $\mu$ is $<1$. In other series, as in the $D$ triplets of Ca, Sr and Ba, the lines corresponding to $m=1$ also occur in the spectra. When satellites are present, an important indication as to the real first member of the $D$ series is given by the equality of the separation of the satellites and those of the components of the $F$ series.

It should be observed that $\mu$ is sometimes rather vaguely regarded as the "phase" of a series, and its values in the series of different elements may be of importance for purposes of comparison in relation to other physical properties of the elements. The correct numeration of the lines determines whether $\mu$ is to be taken as greater or less than unity.

### Enhanced Line Series.

The Rydberg interpolation table may also be used for the preliminary calculation of formulæ for enhanced lines, in which the series constant takes the value $4N$. The intervals between the successive wave-numbers are then to be divided by 4 before taking out the values of $\mu$; and in forming the limits of the series the corresponding adjacent terms have first to be multiplied by 4. The following example from a series of enhanced lines of Mg will sufficiently illustrate the procedure :—

| $\nu$ | $\Delta\nu$ | $\Delta\nu/4$ | $(m+\mu)$ | | $f(m+\mu)$ | $\times 4$ | Limit |
|---|---|---|---|---|---|---|---|
| 12,661 | 10,109 | 2,527 | 3 | 0·965 | 6,976 | 27,904 | 40,565 |
| 22,770 | | | 4 | | 4,449 | 17,796 | 40,566 |

The approximate formula would thus be

$$\nu=40{,}565-4N/(m+0{\cdot}965)^2$$

### Rydberg's Special Formula.

A series of single lines which was identified by Rydberg in the spectrum of magnesium ($D$ in the series tables of Mg) was so imperfectly represented by the ordinary formula that a four-constant formula was adopted—namely,

$$\nu=A-\frac{B}{(m+\mu)^2}-\frac{C}{(m+\mu)^4}$$

where $B$ and $C$ were calculated independently.* Other members of the series have since been recorded, however, and it has been found that the series may be at least equally well represented by the formulæ of Ritz and Hicks, involving only three independent constants, and retaining the hydrogen constant $N$.

It may be noted that the magnesium series in question has not yet been satisfactorily represented by any three-constant formula, and the departure from the formulæ becomes more pronounced in the corresponding singlet series of Ca, Sr and Ba, which belong to the same chemical group.

* Ofversigt af Kongl. Vet.-Akad. Forhandl., Stockholm (1903).

# CHAPTER V.

## OTHER SERIES FORMULÆ.

### RUMMEL.

One of the earliest attempts to improve on the Rydberg formula was that made by Rummel,* who employed a formula which may be written

$$\lambda=\lambda_\infty+\frac{C}{(m+\mu)^2-m_0}$$

where $\lambda_\infty$, $C$, $\mu$ and $m_0$ are constants special to each series.

The same formula, transposed to wave-numbers, was afterwards independently investigated by Fowler and Shaw† in the form

$$\nu=\nu_\infty-\frac{C}{(m+\mu)^2-m_0}$$

and, later, by Halm‡ in the form

$$\frac{1}{\nu_\infty-\nu}=a(m+\mu)^2+b$$

This formula has been shown to represent many individual series with considerable accuracy, but while giving a more convincing proof of the exactness of the laws of limits, it has the disadvantage of not retaining the Rydberg constant, and the calculated term $S(1)$ usually differs widely from $-P(1)$. The formula has, therefore, not much to recommend it, beyond the fact that it admits of an easy direct solution for $(m+\mu)$, and thence for the other constants—namely, that in the second of the above forms—

$$(m_1+\mu)=\sqrt{\frac{a}{a-3}}-1{\cdot}5$$

where $$a=\frac{(\nu_4-\nu_1)(\nu_3-\nu_2)}{(\nu_4-\nu_3)(\nu_2-\nu_1)}$$

and $\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$ refer to four consecutive lines. The formula may, therefore, be of occasional use in the determination of limits.

Halm has attached some importance to the fact that this formula may be transposed into one which is adapted to the series of lines composing band spectra. Thus, if $(m+\mu)$ be put $=0$ in Fowler and Shaw's form of the equation, there results

$$\nu_0=\nu_\infty+\frac{C}{m_0}$$

and, eliminating $\nu_\infty$, it is easily shown that

$$\frac{1}{\nu-\nu_0}=\frac{1}{C}\cdot\frac{m_0^2}{(m+\mu)^2}-\frac{m_0}{C}=\frac{\alpha}{(m+\mu)^2}-\beta$$

or, in terms of wave-lengths

$$\frac{1}{\lambda_0-\lambda}=\frac{\alpha'}{(m+\mu')^2}+\beta'$$

* Proc. Roy. Soc., Victoria, **10**, 75 (1897); **12**, 15 (1899).
† Astrophys. Jour., **18**, 21 (1903).
‡ Trans. Roy. Soc., Edin., **41**, pt. 3, 551 (1905).

The formula represents band series rather better than most of the forms which have been employed, as shown by Halm, and by Fowler in the case of the bands of magnesium hydride.* It is difficult to see, however, what meaning can be attached to such a transposition of the formula.

## Ritz.

An important modification of Rydberg's formula was made by W. Ritz in 1903.† Ritz's formula was to some extent based upon theoretical considerations and took the general form

$$\pm\nu = N\left(\frac{1}{p^2}-\frac{1}{q^2}\right)$$

where $N$ is the Rydberg constant, and $p$, $q$ are the roots of certain transcendental equations which are expressible in the form of the semi-convergent series,

$$p=m+\alpha+\frac{\beta}{m^2}+\frac{\gamma}{m^4}+\ \ldots\ldots$$

$$q=n+\alpha'+\frac{\beta'}{n^2}+\frac{\gamma'}{n^4}+\ \ldots\ldots$$

In the first approximation $p=m+\alpha$, and $q=n+\alpha'$, and the formula becomes identical with that of Rydberg. In a second approximation, for a single series, $N$ being constant,

$$\pm\nu=A-\frac{N}{\left(m+\alpha+\frac{\beta}{m^2}\right)^2}\ \ldots\ldots\ldots\ldots \quad (1)$$

or, in other forms

$$\pm\nu=A-\frac{N}{\left[(m+a)+\frac{b}{(m+a)^2}\right]^2}\ \ldots\ldots\ldots \quad (2)$$

$$\pm\nu=A-\frac{N}{[m+a'-b'(A-\nu)]^2}\ \ldots\ldots\ldots \quad (3)$$

The numeration of the lines adopted by Ritz was not the same as that of Rydberg. In the $P$ series the first line is given by $m=2$, in $D$ by $m=3$, and in $S$ by $m=2{\cdot}5$.

Ritz applied the formulæ (1) and (3) to numerous spectra and showed that they represented the series with much greater accuracy than the three-constant formula of Kayser and Runge. The formulæ also have the advantage of retaining the Rydberg constant for all series, and of satisfying the Rydberg relations between the different series with greater accuracy.

The formula (3) was considered by Ritz to be the most exact, partly on the ground that extrapolation to $m=1{\cdot}5$ in the $S$ formula appeared to give a closer approximation to the first $P$ line than the formula (1). It is doubtful, however, whether the superiority over (1) in this respect is general, and the formula is less convenient in practice.

The Ritz formula in the forms (1) and (3) has been largely employed by Paschen

* Phil. Trans., A, **209**, 460 (1909).

† Ann. der Physik., **12**, 264 (1903). Phys. Zeitschr., **4**, 406 (1903). Gesammelte Werke Walther Ritz ; Œuvres publiées par la Société Suisse de Physique, Paris (1911).

in his admirable and extensive work on series, and the difference in the numeration of the lines as compared with Rydberg should be carefully noted. Thus,

| Series. | Rydberg. | Ritz. |
|---|---|---|
| *P* | 1, 2, 3 . . . | 2, 3, 4. . . . |
| *S* | 2, 3, 4 . . . | 2·5, 3·5 . . . |
| *D* | 2, 3, 4 . . . | 3, 4, 5 . . . |

A consequence of the Ritz numeration is that $\alpha$ is negative, except for series in which the Rydberg figures would give $\mu>1$ in the *P* and *D* series, or $\mu>0{\cdot}5$ in the case of the *S* series.

The Ritz formula in form (1) has been further tested on some of the series of the alkali metals and of helium by R. T. Birge,* who found that while the Kayser and Runge formula, even with four undetermined constants, was inadequate, the Ritz formula, with three undetermined constants and a universal constant, was quite satisfactory for substances of low atomic weight. The agreement with observation, however, became less accurate with the increase of atomic weight, and left much to be desired in the case of cæsium.

The Ritz formula, as pointed out by Birge, has theoretically the form of an infinite series, and the number of terms actually needed to represent a series depends directly upon the magnitudes of the coefficients of the several terms. The coefficients are found to increase with increasing atomic weight, and higher terms of the theoretical series become less negligible in the case of the heavier elements. The following Table given by Birge in this connection for the *P* series of the elements named is instructive :—

| Substance. | Atomic weight. | $\alpha$ | $\beta$ | *A* |
|---|---|---|---|---|
| H | 1 | 0 | 0 | 27419·7 |
| He | 4 | 0·0111 | —0·0047 | 32033·2 |
| Li | 7 | —0·047 | 0·026 | 43482·1 |
| Na | 23 | 0·144 | —0·113 | 41450·1 |
| K | 39 | 0·287 | —0·221 | 35006·5 |
| Rb | 85 | 0·345 | —0·266 | 33689·1 |
| Cs | 133 | 0·412 | —0·333 | 31394·2 |

In the case of Na, the Ritz formula was found to represent the *P* series with special accuracy, and to show that for this element the Rydberg-Schuster law was accurately true. It should be added, however, that atomic weight is not the only factor which influences the accuracy with which a series may be represented by the Ritz formula, or by formulæ of similar type (*see* Chapter VI.).

In a theoretical discussion, Sommerfeld† has arrived at the following generalised form of the Ritz formula :

$$\nu=A-(m,\ a)$$

where $$(m,\ a)=A-\nu=\frac{k^2\,N}{[(m+a)+\alpha(m,\ a)+\alpha'(m,\ a)^2+\ .\ .\ .\ .]^2}$$

For arc spectra, $k=1$, and for enhanced lines $k=2$. This formula has been applied to several series by E. Fues,‡ who also explains a method of determining the constants. For the sharp series of singlets of cadmium ($=2P-mS$ in the Ritz-

* Astrophys. Jour., **32**, 112 (1910).
† "Atombau und Spectrallinien," 2nd Edition, p. 510.
‡ Ann. d. Phys., **63**, 21 (1920).

Paschen system), the constants are $A=28843{\cdot}71$; $a=-0{\cdot}077419$; $\alpha=-1{\cdot}41695\times10^{-6}$; $\alpha'=-1{\cdot}70734\times10^{-11}$; $N=109732{\cdot}7$. The lines of the series, with wave-lengths on Rowland's scale, and the differences $O-C$, are as follows:

| $m$ | 1·5 | 2·5 | 3·5 | 4·5 | 5·5 | 6·5 | 7·5 |
|---|---|---|---|---|---|---|---|
| $\lambda$ | −2288·10 | 10395·17 | 5154·85 | 4306·98 | 3981·92 | 3819 | 3723 |
| $mS$ | 72534·9 | 19226·4 | 9449·8 | 5632·1 | 3737·3 | 2666·4 | 1990·8 |
| $\Delta\lambda$ Paschen | −523 | 0 | −0·8 | 0 | −0·36 | +0·4 | −0·4 |
| $\Delta\lambda$ Fues | 0 | 0 | 0 | +0·02 | −0·3 | +0·4 | −0·3 |

It will be seen that the additional term gives a marked improvement in the representation of the series. About the same accuracy is given by Johanson's formula, to be mentioned later.

### Nicholson's Extension of Ritz Formula.

The higher terms of the second form of the Ritz formula have been taken into account by Nicholson* in a critical comparison of different formulæ for the lines of helium. In this Paper, Nicholson has developed a method of accurately determining the limit of a series having many lines, and has thereby shown that the Rydberg-Schuster law is exact for helium, besides deducing that $N$ has the same value for helium as for hydrogen.† Nicholson also concluded that the most accurate form of the series equation is an extension of that of Rydberg, dependent on $(m+\mu)$ and not upon $m$, namely,

$$\nu=A-\frac{N}{\left[(m+\mu)+\frac{\alpha}{(m+\mu)}+\frac{\beta}{(m+\mu)^2}+\ldots\right]^2}$$

### Lohuizen.

An extensive study of spectral series has been made by Lohuizen,‡ using the formula

$$\nu=A-\frac{N}{(m+\alpha+\beta\nu)^2}$$

It was apparently not recognised that this is equivalent to the Ritz formula no. 3.

### Mogendorff-Hicks.

An extensive and critical study of spectral series has been made by Prof. W. M. Hicks in a series of papers communicated chiefly to the Royal Society.§ The formula which he adopted, while yet unacquainted with the work of Ritz, was

$$\nu=A-\frac{N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}\quad\text{or}\quad\nu=A-\frac{N}{\left(m+\mu+\frac{\alpha}{m}+\frac{\beta}{m^2}\right)^2}$$

* Proc. Roy. Soc., A, **91**, 255 (1915).

† It is possible that the observations were not of sufficient accuracy to justify this conclusion completely.

‡ Bidrage tot de Kennis van Lijnenspectra, Diss. Amsterdam (1912); also Kon. Akad. van Wetenschappen te Amsterdam, June and Sept. (1912) (in English).

§ Phil. Trans., A, **210**, 57 (1910); **212**, 33 (1912); **213**, 323 (1914); **217**, 361 (1918); **220**, 335 (1920).

This formula was found to give even more accurate results than that of Ritz, and it was rarely necessary to go beyond the $\alpha/m$ term. If both $\alpha$ and $\beta$ are included, $\beta$ is only a small fraction of $\alpha$. With $\alpha$ alone the agreement with observation was better than with $\beta$ alone.

The first formula had in fact previously been employed by Mogendorff,* who had applied it successfully to numerous series.

As regards the numeration of the lines, Hicks considers it possible, in the case of a well-observed series, to find the correct order numbers by ascertaining the values which represent the series most perfectly when the above formula is used. Thus, in the $P$ series of the alkalies the denominator ($f$ denoting a fraction) is $[m+(1+f)-\alpha/m]^2$, and not $(m+f-\alpha/m)^2$, for the latter will not reproduce the series within the limits of observational error, and consequently $\mu>1$; in the $S$ series $\mu<1$. This unique determination of $\mu$ is regarded as a matter of the first importance for comparative study, and according to Hicks only fails when the lines are so few, or the measurements so bad, that either $\alpha/m$ or $\alpha/m+1$ will reproduce them within the observational limits. It would seem, however, that this criterion is of somewhat restricted applicability.

In the case of the $S$ series, it was further found by Hicks that the use of $(m+0{\cdot}5)$ in his formula, in place of $m$, made it more difficult to fulfil the Rydberg relations between the $P$ and $S$ series, and he consequently adopted integral values throughout. Thus in general, the Hicks' numeration is identical with that of Rydberg. A special feature of the work of Hicks is the determination of the possible variations in the formulæ constants depending upon the estimated limits of error in the recorded positions of the lines involved.

The Hicks formula seems to have been proved by general experience to be even more accurate than that of Ritz, and it is probably the most generally useful formula which has yet been proposed. The three-constant form is extremely convenient in practice, and well serves the requirements of most series investigations; that is, it serves sufficiently for the identification of lines belonging to a series, and tends to demonstrate the truth of the Rydberg relations. It is not to be expected that it will represent series perfectly. There is usually an outstanding error when it is attempted to include the first line of a series, or in extrapolation to negative terms.

### Paulson.

Two formulæ have been tested on certain series by Paulson,† namely

$$\nu=A-\frac{N}{(m+a)^2}\cdot e^{\frac{b}{m^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

$$\nu=A-\frac{N}{(m+a)^2}\cdot e^{\frac{a}{m^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

the first having three, and the second two, adjustable constants.

Thus, for the $D$ series of lithium, Paulson gives the equations

$$(A) \quad \nu=28588{\cdot}32-\frac{109675\,.\,e^{\frac{0{\cdot}0006631}{m^2}}}{(m+1{\cdot}998672)^2}$$

$$(B) \quad \nu=28593{\cdot}13-\frac{109675\,.\,e^{-\frac{0{\cdot}003497}{m^2}}}{(m-0{\cdot}003497)^2}$$

* Dissertation, Amsterdam (1906).

† Kongl. Fysiog. Sällsk. Handlingar N.F., Bd. 25, No. 12 (1914) (in German).

In $(A)$, $m$ has the values 1, 2, 3, . . . . ; and in $(B)$ 3, 4, 5, . . . . The order of accuracy resulting from the formulæ may be gathered from the appended table, in which the residuals are compared with those given by Lohuizen (Ritz formula), by Kayser and Runge, and by Mogendorff :—

| $m$ | λ Obs. | $\Delta A$ | $\Delta B$ | $\Delta L$ | $\Delta KR$ | $\Delta M$ |
|---|---|---|---|---|---|---|
| 1..... | 6103·77 | (0) | (0) | (0) | (0) | (0) |
| 2..... | 4602·37 | (0) | (0) | (0) | (0) | (0) |
| 3..... | 4132·44 | —0·02 | +0·31 | (0) | (0) | —0·11 |
| 4..... | 3915·2 | —0·18 | +0·28 | —0·25 | —0·20 | (0) |
| 5..... | 3794·9 | —0·29 | +0·24 | —0·40 | —0·35 | +0·09 |
| 6..... | 3718·9 | —2·16 | —1·61 | —2·30 | —2·25 | —1·94 |
| 7..... | 3670·6 | —1·30 | —0·72 | —1·45 | —1·41 | —1·06 |

It does not seem that Paulson's formulæ have any special advantage over the Ritz' or Hicks' formulæ, and the relation $S(1)=-P(1)$, which is so important in the Rydberg system, has not been taken into consideration.

## JOHANSON.

A study of numerous series has been made by Dr. A. M. Johanson,* using a formula which may be written as follows in the notation adopted in the present report :—

$$\nu=A-\frac{N}{\frac{1}{4}[\sqrt{(m+\mu)^2+a}+\sqrt{(m+\mu)^2+b}]^2}$$

It will be seen that if $a=b=0$, and $\mu$ is an integer, the formula reduces to that of Balmer for hydrogen ; while if $\mu$ be a fraction it becomes identical with that of Rydberg. When $a=b$, the formula becomes identical with that of Rummel, in the form given by Fowler and Shaw, except that the Rydberg constant $N$ is generally retained. Johanson's formula may thus be regarded as a more general form of the Rummel formula. For some series the constants $a$ and $b$ have imaginary values.

By development in series, Johanson has also shown that the formula includes the formulæ of Kayser and Runge, and Rydberg's more general formula as special cases, and the relation to the formulæ of Ritz and Hicks is also indicated. The numeration of the lines in a series begins with zero for the first member.

In nearly all cases Johanson has adopted the hydrogen constant for $N$, and has usually assumed the truth of the Rydberg laws in deducing the limits of series belonging to the same system. But in the case of the $D$ series of aluminium, which has always been difficult to represent by formulæ adapted to other series, the value of $N$ has been independently calculated, giving the following constants for the less refrangible components :—

$N=80858$ $A=48071·89$
$\mu=0·538853$ $a=17·269197$ $b=-0·173823$

It is concluded that in this series $N$ cannot have the same value as the Rydberg constant calculated from hydrogen. It should be noted, however, that even the five-constant formula does not represent the nine lines of the series with an accuracy equal to that of the observations, the error reaching 0·41 $A$ in the case of one of

* Arkiv. för Mat., Ast. och Fysik., Band 12, No. 6 (1917) (in German).

the lines, so that the series can scarcely be used to justify the assumption of a real change in $N$.

In the majority of cases the Johanson formula, with four adjustable constants, appears to be very successful. A notable improvement appears in the representation of the diffuse singlet series of magnesium. This series was considerably extended by Fowler and Reynolds,* who deduced the following formula from wave-lengths on the Rowland scale :—

$$\nu = 26618{\cdot}20 - \frac{109675}{(m + 0{\cdot}314582 + 0{\cdot}899929/m - 0{\cdot}269730/m^2)^2}$$

Johanson's constants are—

$$A = 26621{\cdot}00 \qquad \mu = 1{\cdot}283559$$
$$a = 4{\cdot}638975 \qquad b = 0{\cdot}281555$$

The respective results from the two formulæ are shown in the following table :—

| Order number in $J$. | Authority. | Limit of Error. | λ (Rowland scale). | $\nu$ | λ Obs.—λ calc. | |
|---|---|---|---|---|---|---|
| | | | | | F. & R. | $J$. |
| 0 | Paschen | 1·00 | —17108·1 | —5843·61 | 24903 | 0·00* |
| 1 | Hermann | — | 8806·96 | 11351·59 | +142·5 | 0·00* |
| 2 | Rowland | — | 5528·641 | 18082·68 | 0† | —0·48* |
| 3 | ,, | — | 4703·177 | 21256·37 | 0† | +0·55* |
| 4 | ,, | — | 4352·083 | 22971·14 | 0† | —0·11 |
| 5 | F. & R. | 0·02 | 4167·55 | 23988·25 | —0·1 | —0·36 |
| 6 | ,, | 0·02 | 4057·78 | 24637·17 | —0·3 | —0·50 |
| 7 | ,, | 0·02 | 3986·94 | 25074·91 | —0·4 | —0·54 |
| 8 | ,, | 0·03 | 3938·58 | 25382·79 | —0·4 | —0·50 |
| 9 | ,, | 0·05 | 3904·17 | 25606·50 | —0·3 | —0·27 |
| 10 | ,, | 0·05 | 3878·73 | 25774·45 | —0·1 | —0·08 |
| 11 | ,, | 0·10 | 3859·39 | 25903·60 | 0† | +0·11 |

The lines marked * and † were respectively used in the calculation of constants.

It will be seen that Johanson has been able to include the first two lines of the series, and to extrapolate to the 12th member without introducing large errors. Paschen, however, does not now consider the first line to belong to the series. It is clear, nevertheless, that this series cannot be correctly represented by either of the formulæ. It may well be included with the $D$ series of aluminium as among the best examples with whcih to test any proposed new formula.

Johanson considers that his formula not only gives a good agreement between the calculated and observed wave-numbers for series which have been found to be well represented by other formulæ, but also gives good agreement in other cases, and has the special advantage that lines with the smallest order-numbers may be used in the calculation of limits. Also, the change from real to imaginary values of the wave-number given by the formula when $m$ takes the values 1, 0, —1, provides a means of determining the true first line (" grundlinie ") of the series, and thence also the true order-numbers.

The method of calculating the constants is indicated in the Paper, but cannot usefully be abstracted. The process is less tedious than might be supposed.

* Proc. Roy. Soc., A., **89**, 142 (1913).

ISHIWARA.

In an extension of Bohr's theory of spectra, J. Ishiwara* has deduced a general series formula which, for arc spectra, may be written

$$\nu = A - \frac{N}{(m+\mu)^2[1+\alpha(A-\nu)+\beta(A-\nu)^{\frac{3}{2}}]} - \frac{N\sigma}{(m+\mu)^4}$$

$N$ is the Rydberg constant, adapted for the element as in Bohr's theory (chap. IX.), and $\sigma$ is a constant representing $3\pi^2e^4/4c^2h^2$, where $e$ is the unit electric charge, $h$ is Planck's constant, and $c$ is the velocity of light. The last term is a relativity correction. For enhanced spectra, $N$ and $\sigma$ are to be multiplied by 4.

The formula was applied by Ishiwara to the various enhanced series of magnesium and showed a close agreement with the observations. These series are also closely represented by the formulæ of Ritz or Hicks, but in the case of the $\lambda$4481 series (with $\beta=0$) there appears to be a definite improvement. The formula does not yet appear to have been tested on series of other elements.

* Math. and Phys. Soc., Tokyo, Series 2, 9, 20 (1916).

# CHAPTER VI.

## "ABNORMAL" SERIES.

### Intensities.

For the sake of simplicity the foregoing description of the properties of series lines has been restricted chiefly to the most generally occurring cases. Some of the rules which have been stated, however, are not of universal application.

In general, the intensities show a gradual decrease in passing to the higher members of a series, but there are a few cases in which the sequence of intensities is irregular. A well-known example is the very feeble appearance of the second member of the diffuse series of potassium ($\lambda$6966), although succeeding pairs decline in regular order. The second member of the $P$ singlet series of calcium, $\lambda$2721, is also unduly faint as compared with the preceding very intense line at 4227, and the following line at 2398. Other examples are found in the diffuse series of calcium triplets.

### Satellites.

The laws which have been stated with regard to the arrangement of satellites are also sometimes departed from. The diffuse series of aluminium provides an example in the case of a doublet series. Good measurements of these lines in I.A. have been made by Grunter,* from which the following may be derived for the wave-numbers of the chief line and satellite, $\delta_{11}$ and $\delta_{12}$, and the second line $\delta_2$ :—

| $\delta_{12}$ | $\delta_{11}-\delta_{12}$ | $\delta_{11}$ | $\delta_2-\delta_{12}$ | $\delta_2$ |
|---|---|---|---|---|
| 32323·36 | 1·34 | 32324·70 | 112·04 | 32435·40 |
| 38817·13 | 4·49 | 38821·62 | 112·05 | 38929·18 |
| 42121·47 | 4·05 | 42125·52 | 112·03 | 42233·50 |
| 44054·51 | 2·31 | 44056·82 | 112·09 | 44166·60 |

The separation of the satellite and chief line does not regularly diminish as in the normal cases, and the constancy of the distance from the satellite to the second chief line shows that it is the first chief line which is irregular, and not the satellite. The $\varphi$ series lies in the infra-red, and the separation of the two components is not known.

The recent very complete investigations of the spectra of Ca, Sr and Ba which have been made by Saunders have also shown marked irregularities in the arrangement of the satellites in the diffuse series of these elements (*see* tables).

### Spacing of Lines.

Another kind of abnormality takes the form of an unusual spacing of the lines of a series, so that the ordinary series formulæ will not represent them with any reasonable approach to the accuracy of the observations. The singlet series of magnesium to which reference has already been made (p. 37) is one of the best known examples, but more extreme cases have been found by Saunders in the corresponding singlet series of Ca, Sr and Ba. The $\delta$ series of aluminium doublets and the $\sigma$ series of thallium are also well-known examples.

* Zeit. Wiss. Phot., **13**, 1 (1914).

Rydberg's simple formula utterly fails to represent such series, and though a great improvement results in some cases from the introduction of another constant, as in the formulæ of Ritz or Hicks, it is evident that some more drastic change in the formula is necessary. The study of these extreme cases is clearly of great importance, since very few series can be considered to be perfectly represented by the ordinary formulæ, and if a general formula be possible the abnormal series would seem to provide the most suitable data for its investigation.

The nature of the abnormality will be partially gathered from a comparison with a more normal series, say the $P$ singlet series of Ca with the $P$ series of He. The wave-numbers of the first nine lines of each of these series are given below, together with the values of $\mu$ taken from Rydberg's table :—

| | Ca (singlet $P$). | | | He (doublet $P$). | | |
|---|---|---|---|---|---|---|
| $m$ | $\nu$ | $\Delta\nu$ | $\mu$ | $\nu$ | $\Delta\nu$ | $\mu$ |
| 1 | 23,652 | | | 9,231 | | |
| | | 13,080 | 1·12 | | 16,477 | 0·939 |
| 2 | 36,732 | | | 25,708 | | |
| | | 4,947 | 1·09 | | 5,652 | 0·934 |
| 3 | 41,679 | | | 31,360 | | |
| | | 2,254 | 1·14 | | 2,584 | 0·933 |
| 4 | 43,933 | | | 33,944 | | |
| | | 1,492 | 0·81 | | 1,392 | 0·932 |
| 5 | 45,425 | | | 35,336 | | |
| | | 1,055 | 0·45 | | 834 | 0·932 |
| 6 | 46,480 | | | 36,170 | | |
| | | 705 | 0·30 | | 540 | 0·930 |
| 7 | 47,185 | | | 36,710 | | |
| | | 476 | 0·25 | | 368 | 0·93 |
| 8 | 47,661 | | | 37,078 | | |
| | | 338 | 0·18 | | 264 | 0·93 |
| 9 | 47,999 | | | 37,342 | | |

It will be seen that in the He series the successive values of $\mu$ change very slowly and regularly, whilst in the Ca series they change so rapidly that Rydberg's table would not serve to indicate the positions of succeeding lines with any certainty.

The imperfect representation of this series by formulæ will be gathered from the observed *minus* computed wave-numbers given in the accompanying table, the formulæ employed being as follows :—

I. $\nu=49{,}148-N/[m+0{\cdot}870+0{\cdot}204/m]^2$.

II. $\nu=49{,}216-N/[m+0{\cdot}345+1{\cdot}750/m-1{\cdot}024/m^2]^2$.

III. $\nu=49{,}305-164{,}970/[m+1{\cdot}708666-0{\cdot}172761/m]^2$.

IV. $\nu=49{,}305-N/[m+1{\cdot}528649+2{\cdot}774349/m-1{\cdot}190193e^{\frac{1}{m}}]^2$.

V. $\nu=49{,}305-N/[m+0{\cdot}126879+6{\cdot}620605/m^2-5{\cdot}679767/m^4]^2$.

VI. $\nu=49{,}305-N/[m-1{\cdot}092198+17{\cdot}291194/m^2-50{\cdot}606112/m^4]^2$.

VII. $\nu=49{,}305-N/\frac{1}{4}[\sqrt{(m+0{\cdot}180653)^2+23{\cdot}351373}+\sqrt{(m+0{\cdot}180653)^2+0{\cdot}457737}]^2$.

VIII. $\nu=49{,}376-N/\frac{1}{4}[\sqrt{(m+0{\cdot}100167)^2+23{\cdot}882095}+\sqrt{(m+0{\cdot}100167)^2+0{\cdot}564884}]^2$.

The limit given by Saunders (49,305) has been adopted in all but the first two and the last formulæ, and in all cases the lines used in the calculation of constants

are marked by an *. In III., $N$ has been independently calculated. In VI., the lines have been numbered 2, 3, 4 . . . in place of 1, 2, 3 . . . Formula IV. was suggested by the forms first used by Paschen for certain series in the spectrum of neon, none of which, however, appear to be adapted to the Ca series under discussion. Paschen afterwards found that such formulæ were not required for the neon series. The last two formulæ are in Johanson's form, one with the limit assumed, and the other with the limit calculated.

*Calcium, Singlet P Series.*

| $m$ | $\lambda$ | $\nu$. | I. | II. | III. | IV. | V. | VI.† | VII.§ | VIII.§ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4226·73 | 23652 | +2* | +8* | 0* | 0* | * | 0* | 0* | 0* |
| 2 | 2721·65 | 36732 | +1* | 0* | 0* | 0* | —3234 | —1892 | —1642 | —1735 |
| 3 | 2398·58 | 41679 | —397 | 0* | 0* | 0* | * | +6* | 0* | 0* |
| 4 | 2275·49 | 43933 | —686 | —357 | —232 | —394 | * | 0* | 0* | 0* |
| 5 | 2200·76 | 45425 | —584 | —361 | —176 | —303 | —92 | —44 | +6 | —8 |
| 6 | 2150·78 | 46480 | —367 | —223 | — 28 | —244 | —67 | —6 | +71 | +42 |
| 7 | 2118·68 | 47185 | —205 | —119 | + 68 | —197 | —39 | +16 | +98 | +59 |
| 8 | 2097·49 | 47661 | —101 | —54 | +114 | —135 | —24 | +22 | +99 | +51 |
| 9 | 2082·73 | 47999 | —28 | —8 | +138 | —92 | —12 | +26 | +93 | +40 |
| 10 | 2073·04 | 48223 | 0* | 0* | +125 | —85 | —25 | +5 | +62 | +5* |
| 11 | 2064·77 | 48416 | +44 | +30 | +135 | —56 | —12 | +13 | +63 | —2 |

† Numeration begins with $m=2$.

§ Numeration begins with $m=0$; and for the first line the *difference* of the two terms inside the brackets has to be taken.

The results of the calculations do not clearly suggest that the necessary modification of the ordinary formulæ is to be found in a change of the value of the series constant. As already remarked, however, in the case of the $\delta$ series of aluminium, Johanson found it impossible to represent the lines by his formula without making such a change; he deduced a value of about 80,000 for this series in place of the usual 109,678, and found a fair representation of the lines. The constant $a$ in the formula then had the very large value 17·3, as compared with values which rarely exceed 2 for most series, while $b$ was small. Ca $P$ has the same features in greater degree.

A part of the difficulty of representing an abnormal series such as that of the Ca $P$ singlets appears to arise from a difference in the rates of convergence of the earlier and later lines. Lorenser* and Saunders have illustrated this as in Fig. 7. If the series equation be of the form

$$\nu=A-\frac{N}{[m+\mu+f(m)]^2}$$

we have

$$f(m)=\sqrt{\frac{N}{A-\nu}}-(m+\mu).$$

If $N$ be assumed, and a value of $A$ be assigned from a consideration of the later lines of the series, $f(m)$ will represent what Saunders has called "the residual," and the curve is drawn by plotting the residual, or $\mu+f(m)$ against $m$. It will be seen that the curve has a point of inflexion in the part corresponding to the earlier members, so that the residual cannot be a very simple function of $m$.

* Beiträge zur Kenntnis den Bogenspektren der Erdalkalien. Dissertation, Tübingen (1913), p. 41.

The curve represents the Ca singlet $P$ series, $A$ having been taken as 49,305; the values of $\mu+f(m)$ for the eleven lines are

| | |
|---|---|
| (1) 1·0677 | (7) 0·1927 |
| (2) 0·9535 | (8) 0·1679 |
| (3) 0·7924 | (9) 0·1641 |
| (4) 0·5185 | (10) 0·0681 |
| (5) 0·3167 | (11) 0·1073 |
| (6) 0·2309 | |

Similar results are shown also by the corresponding singlet series of strontium and barium, and also for the $d$ series of calcium triplets and the $f$ series of barium, particulars of which will be found in the general tables.

It will be evident that the representation of series by formulæ is a subject which is far from having been exhausted, and that the "abnormal" series to which

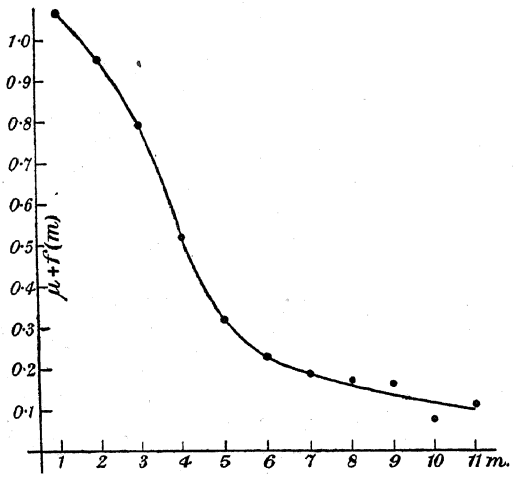


FIG. 7.—CURVE OF $\mu+f(m)$ FOR THE Ca SINGLET PRINCIPAL SERIES.

attention has been directed furnish valuable material for further investigations. The simpler formulæ which represent many of the series very closely are evidently only approximate, and cease to be of use in extreme cases. They would seem to be merely first approximations to a more general formula which may be applicable to all series. Until some such formula has been found, it would seem that some interesting questions, such as that of the approximate constancy of $N$ for different elements, cannot be completely investigated.

Meanwhile, in investigations connected with combination series, as already explained, the use of a formula can be dispensed with. The limit of one of the main series having been calculated, the other limits are derived by the Rydberg-Schuster and Runge laws, and "terms" are formed for the lines by subtracting the wave-numbers from the limits of the series to which they belong. The combinations of the terms may then be compared with the wave-numbers of other observed lines.

# CHAPTER VII.

## SPECTRA AND ATOMIC CONSTANTS.

### General Relationships.

Following the classification of spectral lines in series, it was natural to seek for relations between the series spectra of different elements. Hartley* and others had, in fact, previously noted similarities in the spectra of related elements, such that one spectrum might to some extent be considered to be produced by displacing another bodily through a certain distance. It is interesting to note that in this connection Hartley found " a considerable body of evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous ; or, in other words, are the same kind of matter in different states of condensation."

The early work of Rydberg, and that of Kayser and Runge, indicated two definite influences of atomic weight upon the respective series spectra :—

(1) In elements of the same chemical group, the limits of corresponding series advance towards the red with increasing atomic weight.

(2) In elements of the same group, the wave-number separations of doublets or triplets in corresponding series are roughly proportional to the squares of the atomic weights.

These results are illustrated diagrammatically for the sharp triplet series of Mg, Ca, Sr and Ba in Fig. 8.

Rydberg also drew attention to the approximate constancy of the sums of the constants $\mu$ in his formulæ for the sharp and diffuse series in the spectra of elements of the same group and of their differences in corresponding elements of Groups II. and III. These relations, however, are very rough, and a similar examination of the constants of the Hicks formulæ has not led to any significant results.

### Limits and Atomic Weights.

The general relation between the limits of corresponding series in elements of the same group is illustrated in the following table :—

| Doublets | $\pi_\infty$ | $\sigma_{1\infty}$ | Doublets | $\pi_\infty$ | $\sigma_{1\infty}$ | Triplets. | $p_\infty$ | $s_{1\infty}$ |
|---|---|---|---|---|---|---|---|---|
| Li ..... | 43,486 | 28,582 | O ..... | 33,043 | 21,207 | Mg ..... | 20,474 | 39,760 |
| Na ..... | 41,449 | 24,476 | S ..... | 31,148 | 20,085 | Ca ..... | 17,765 | 33,989 |
| K ..... | 35,006 | 21,963 | Se..... | 30,699 | 19,268 | Sr..... | 16,898 | 31,038 |
| Rb ..... | 33,689 | 20,873 | | | | Ba ..... | 15,869 | 28,515 |
| Cs..... | 31,405 | 19,672 | | | | | | |

In the case of the alkali metals, if the limits of the subordinate series and the atomic weights be taken as co-ordinates, the points lie on a fairly regular curve, except as regards $K$ ; or, if the logarithms of the two sets of figures be plotted, the points will lie nearly on a straight line, with $K$ again out of order. The Ca group shows similar results, with Ca discordant.

The limits of the principal series, however, are less regularly connected with the atomic weights than those of the subordinate series.

* Jour. Chem. Soc., **43**, 390.

## Limits and Atomic Volumes.

A possible relation between the limits of the subordinate series and the atomic volumes of the elements appears to have been first suggested by Reinganum.* If the atomic volumes of the elements of Group II. were divided by 4, and those of Group III. by 6, while those of Group I. retained their ordinary values, Reinganum found that when the logs. of the modified atomic volumes were plotted against the logs. of the limits of corresponding series, the points for *all* the elements considered fell approximately on a straight line. The relation, however, is by no means precise.

From the consideration that the wave-frequencies of the transverse vibrations of an elastic body are inversely proportional to the linear dimensions (or to the cube roots of the volumes), and that some similar relationship might be found for vibrating atoms, Halm† also suggested a possible relation between the limits of series and the

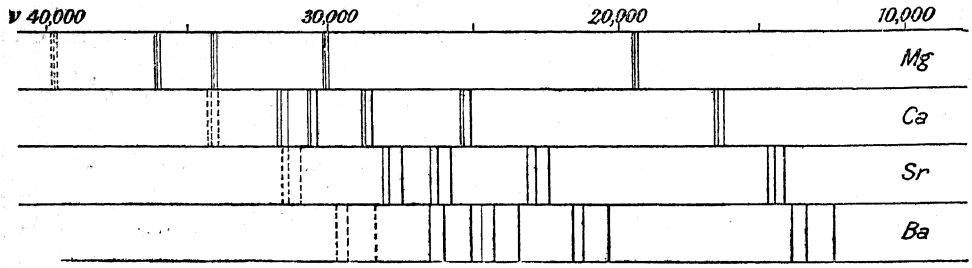


Fig. 8.—The Sharp Series of Mg, Ca, Sr, Ba, showing Influence of Atomic Weight.

atomic volumes of the elements. For elements of the same group, Halm found that the limits of the subordinate series were approximately represented by an equation of the form

$$S_\infty = a + bv^{-\frac{1}{3}}$$

where $v$ is the atomic value and $a$ and $b$ are constants. Thus, the alkali group was represented with $a=9{,}934$, $b=42{,}300$; Zn, Cd, Hg with $a=24{,}228$, $b=38{,}960$; and so on. The approximate relation, however, was not fulfilled for the group Al, In, Tl. As in the case of the atomic weights, the limits of the principal series of the alkalies failed to show the same simplicity as those of the subordinate series; a fair agreement, however, was obtained by making $a=34{,}610$ and $b=2\times10^4$ for Li and Na, and $a=12{,}758$, $b=8\times10^4$ for K, Rb, Cs.

The possible atomic volume relationship has also been considered by Birge,‡ who found that the constants of the Ritz formulæ for the principal series of the alkali metals were roughly proportional to the atomic volumes, as shown in the following table:—

| Element. | $a$ | $b$ | $b/a$ | At. vol. | $a$/at. vol. | $b$/at. vol. |
|---|---|---|---|---|---|---|
| Na ..... | 0·14433 | —0·11302 | 0·784 | 23·606 | $613\times10^{-5}$ | $480\times10^{-5}$ |
| K ..... | 0·28692 | —0·22083 | 0·770 | 44·617 | $642\times10^{-5}$ | $495\times10^{-5}$ |
| Rb ..... | 0·34559 | —0·26577 | 0·768 | 56·05 | $627\times10^{-5}$ | $473\times10^{-5}$ |
| Cs ..... | 0·41196 | —0·33269 | 0·807 | 70·584 | $585\times10^{-5}$ | $472\times10^{-5}$ |

* Phys. Zeit., **5**, 302 (1904).
† Trans. Roy. Soc., Edin., **41**, 593 (1905).
‡ Astrophys. Jour., **32**, 123 (1910).

It is doubtful if anything more significant is to be gained from comparisons of the formulæ constants than from direct discussions of the limits of the subordinate series, since the latter are determined by the constants of the principal series.

In the case of the alkali metals, there is certainly a great improvement in the representation of potassium when atomic volumes are substituted for atomic weights in the construction of a curve showing the relation with the limits of the subordinate series. In the alkaline-earth group, however, strontium is notably discordant, as may be observed by plotting the following figures :—

| Element. | $s_{1\infty}$ | At. vol. |
|---|---|---|
| Mg..... | 39,752 | 14·0 |
| Ca ..... | 33,983 | 25·5 |
| Sr ..... | 31,026 | 34·5 |
| Ba ..... | 28,575 | 36·63 |

Further data for the consideration of these questions may be derived from the general tables of spectra which form part of this Report.

## Doublet and Triplet Separations.

The following extract from a table given by Rydberg* will illustrate the approximate relation between the separations of doublets and triplets and the squares of atomic weights in elements of the same group.†

| | At. wt. | $\Delta\nu$ or $\Delta\nu_1$ | $10^3\Delta\nu/W^2$ |
|---|---|---|---|
| Li‡ | 7·03 | — | — |
| Na | 23·06 | 17·19 | 32·3 |
| K | 39·14 | 57·85 | 37·8 |
| Rb | 85·44 | 235·98 | 32·3 |
| Cs | 132·88 | 553·87 | 31·6 |
| Zn | 65·38 | 388·97 | 91·0 |
| Cd | 112·08 | 1170·76 | 93·2 |
| Hg | 200·36 | 4631·17 | 115·4 |

| | At. wt. | $\Delta\nu$ | $10^3\Delta\nu/W^2$ |
|---|---|---|---|
| Cu | 63·44 | 248·54 | 61·8 |
| Ag | 107·94 | 920·48 | 79·0 |
| Au | 197·25 | 3815·40 | 98·1 |
| Al | 27·08 | 112·02 | 152·8 |
| Ga | 69·9 | 823·6 | 168·6 |
| In | 113·4 | 2212·54 | 172·1 |
| Tl | 204·15 | 7792·63 | 187·0 |

It will be seen that the proportionality between $\Delta\nu$ and $W^2$ in the same group is only very roughly given by the equation

$$\Delta\nu = kW^2, \text{ or } W = c(\Delta\nu)^{\frac{1}{2}}$$

A closer agreement was found by Runge and Precht§ by using the equation

$$W = C(\Delta\nu)^n$$
$$\text{or } \log W = \log C + n \log (\Delta\nu)$$

Thus, it was found that by taking logs. of the atomic weights and logs. of the separations as co-ordinates, the points representing elements of the same group lie nearly on a straight line. In an attempt to determine the atomic weight of radium from the spectroscopic data, Runge and Precht discussed the enhanced doublets of the calcium group, for which the equation becomes

$$\log W = 0{\cdot}2005 + 0{\cdot}5997 \log \Delta\nu$$

* Rapp. au Congrès Int. de Phys., Paris (1900).

† Note.—Rydberg and some other writers have represented separations by $\nu$, but, as this is more appropriate to wave-numbers, $\Delta\nu$ is here adopted for the separations of doublets and triplets.

‡ The separation 0·34 given by Kent is out of step with $\Delta\nu$ for the other alkali metals.

§ Phys. Zeit, **4**, 285 (1903) ; Phil. Mag., **5**, 476 (1903).

The results are shown in the following table :—

| | $\Delta\nu$ | $W$ | $W$ calc. | $O-C$ |
|---|---|---|---|---|
| Mg | 91·7 | 24·36 | 23·84 | +0·52 |
| Ca | 223·0 | 40·1 | 40·6 | —0·5 |
| Sr | 801·0 | 87·6 | 87·5 | +0·1 |
| Ba | 1691·0 | 137·4 | 136·9 | +0·5 |
| Ra | 4858·5 | 225·0 | 258·0 | —33·0 |

The result for Ra is much too high, and it is evident that the formula is not sufficiently exact for the long extrapolation required. A variation in procedure was adopted by Rudorf,* who plotted curves for the different groups with $100\Delta\nu/W^2$ and $W$ as co-ordinates. The curves were rather complex, but appeared to pass in all cases through the zero point. No calculations were given, and the method does not appear to lend itself to such an extrapolation as that required for radium.

Using Runge and Precht's data, Dr. Marshall Watts† derived an interpolation formula for the enhanced doublets of the calcium group, namely,

$$\log W = 1{\cdot}886242 + 0{\cdot}623179a - 0{\cdot}080391a^3 - 0{\cdot}0374175a^4$$

where $$a = \log \Delta\nu - 2{\cdot}813121$$

The calculated atomic weights were Mg 24·32, Ca 40·08, Sr 87·62, Ba 137·41, Ra 226·56, in close agreement with the true values. It will be observed, however, that the formula involves as many constants as there are elements in the group.

A further attempt to determine the atomic weight of radium was made by the Misses Anslow and Howell,‡ using the separations of the extreme members of triplets which they believed they had identified in radium, and comparing them with corresponding terms for other elements of the group. The logs. of the separations and logs. of the atomic weights gave points which lay very nearly on a straight line, and indicated 231·7 for the atomic weight of radium.

The separations of doublets and triplets were discussed by Ritz in a different way.§ Thus, the main separation in a doublet system in our notation is given by $\sigma_2\infty - \sigma_1\infty$, and from the relation between the $\sigma$ and $\pi$ series we have

$$\Delta\nu = \sigma_2\infty - \sigma_1\infty = N/(1+\pi_2)^2 - N/(1+\pi_1)^2$$

where $\pi_2$ and $\pi_1$ may include extra terms introduced for the better representation of the series. In the Ritz formulæ, the denominator terms are indicated by $(m+p_1+\pi'/m^2)$ and $(m+p_2+\pi''/m^2)$, and Ritz found that the quantities $(p_1-p_2)$ gave a much smaller range of values in relation to the squares of the atomic weights than did the separations themselves when different groups of elements were included in the comparison. His results are shown in the following table :—

| | Na | K | Rb | Cs | Cu | Ag | Mg | Ca | Sr | Zn | Cd | Hg | Al | In | Tl | He |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta\nu_1.10^3/W^2$ | 32·3 | 37·8 | 32·2 | 31·6 | 61·8 | 79·0 | 68·8 | 66·1 | 51·5 | 91·0 | 93·2 | 115·4 | 152·8 | 172·1 | 187·0 | 63·8 |
| $\frac{p_1-p_2}{W^2}.10^7$ | 14·2 | 18·9 | 18·0 | 18·6 | 18·6 | 24·2 | 14·6 | 17·7 | 15·7 | 17·2 | 18·6 | 22·3 | 24·8 | 29·2 | 32·7 | 20·4 |

* Zeit. Phys. Chem., **50**, 100 (1904).
† Phil. Mag., **18**, 411 (1909).
‡ Proc. Nat. Acad. Sci., Wash., **3**, 409 (1917).
§ Astrophys. Jour., **28**, 241 (1908); **29**, 243 (1909).

The essential difference of procedure as compared with the use of direct values of $\Delta\nu$ is that in the form $(p_1-p_2)$ the doublet or triplet separations are associated with the limits of the subordinate series. Ritz regarded these results as merely preliminary, but does not appear to have carried the matter further. A more exhaustive study, however, has been made by Hicks (*see* Chapter VIII.).

The results obtained by substituting atomic volumes for atomic weights in relation to the doublet and triplet separations in the foregoing comparisons do not appear to be any more definite than those already quoted. Thus, in the elements of the alkali group, potassium still deviates from the curve which connects atomic volumes with the separations, or from the straight line when the logarithms are plotted.

### Homologous Lines and Atomic Weights.

In an attempt to discover the relations between the spectra and other physical properties of the elements, Ramage* compared graphically the corresponding or "homologous" lines in the different elements of the various groups. The characteristic flame lines Mg 2852, Ca 4227, Sr 4607, Ba 5535, are examples of such lines; and, in general, lines of corresponding series which have the same value of $m$ would be regarded as homologous. Such lines, like the limits of the series to which they belong, usually advance towards the red with increase of atomic weight. The curves connecting their wave-numbers with the atomic weights, or with the squares of the atomic weights, however, were found by Ramage not to be continuous throughout the whole of a group of elements. In the alkalies, for instance, there was a break between Na and K. It does not seem probable that the discussion of individual lines will lead to more definite relations than those of the limits of the series.

Ramage also derived empirical formulæ for the series of K, Rb and Cs, in which the atomic weight was the only variable, apart from the parameter $m$. Thus, he found that the second components of the principal series were given by

$$\nu=35{,}349-0{\cdot}2233W^2-N/[m+1{\cdot}19126+0{\cdot}00103W+(0{\cdot}04377+13W^2\times10^{-7})(1-3^{1-m})]^2.$$

The possibility of obtaining such a formula strongly suggested to Ramage that the differences between the series of the three elements in question depended solely upon differences of atomic weights. The number of constants involved, however, is too large to give confidence in such a conclusion, especially as the formula fails to include lithium and sodium.

Other relationships between homologous lines and atomic weights were afterwards suggested by Marshall Watts.† Thus, in each of the two groups K, Rb, Cs, and Ca, Sr, Ba, the differences of wave numbers between corresponding lines in their spectra were found to be nearly proportional to the differences between the squares of the atomic weights. In the first group the lines having the following wave-numbers were assumed to be homologous :—

| | Cs | | Rb | | K |
|---|---|---|---|---|---|
| (*a*) | 12,469 (6) | ... | 13,742 (4) | ... | 14,465 (7) |
| (*b*) | 21,764 (6) | ... | 23,714 (6) | ... | 24,700 (6) |
| (*c*) | 21,945 (8) | ... | 23,791 (8) | ... | 24,719 (8) |
| | &c. | | &c. | | &c. |

* Proc. Roy. Soc., **70**, 1 and 303 (1901-02).
† Phil. Mag., (6) **5**, 203 (1902).

Adopting atomic weights 132·7 for **Cs** and 39·9 for **K**, the rule gives with lines (*a*) 86·87, with lines (*b*) 83·24, and with lines (*c*) 83·11 for the atomic weight of Rb (85·2). The limits of the principal series, treated in the same manner, give 86·0. Reference to the general tables will show that the lines (*a*) are not homologous, and if the correct line of Cs(13,138) be introduced the deduced atomic weight for **Rb** becomes 102. The suggested relation also excludes lithium and sodium and would therefore seem to have no great significance.

In another class of elements, represented by Zn, Cd, Hg and Ga, In, Watts found that the differences between the wave-numbers of certain lines of one element were to the differences between the corresponding lines of the other elements as the squares of their atomic weights. Among the pairs of assumed corresponding lines of **Cd** and **Zn** given by Watts are the following :—

| | Cd | | Zn |
|---|---|---|---|
| (*a*) | 30654·4 (10) | ..... | 32500·0 (8) |
| (*b*) | 30734·9 (8) | ..... | 32540·1 (10) |
| (*c*) | 31905·5 (8) | ..... | 32928·7 (10) |
| (*d*) | 32446·8 (6) | ..... | 33118·6 (8) |
| | &c. | | &c. |

The assumption of 111·83 for the atomic weight of **Cd** then gives 65·44 from (*a*) and (*c*), 65·69 from (*a*) and (*d*), and so on, for that of **Zn** (64·9). Since lines (*b*), (*c*) and (*d*) belong to corresponding triplets, and lines (*a*) are not placed in series, it will be seen that in place of taking the triplet separations themselves to be proportional to the squares of the atomic weights, Watts has added wave-numbers to the separations equal to the intervals between the lines (*a*) and (*b*) of the two elements. That is, since $(c)-(b)=\Delta\nu_1$, and $(d)-(c)=\Delta\nu_2$, if $(b)-(a)$ be called $x$ for **Cd** and $y$ for **Zn**, Watts makes—

For (*a*) and (*c*) $$\frac{x+\Delta\nu_1}{y+\Delta\nu_1'}=\frac{(\mathrm{Cd})^2}{(\mathrm{Zn})^2}$$

and for (*a*) and (*d*) $$\frac{x+\Delta\nu_1+\Delta\nu_2}{y+\Delta\nu_1'+\Delta\nu_2'}=\frac{(\mathrm{Cd})^2}{(\mathrm{Zn})^2}$$

The difference between the two results from members of undoubtedly corresponding triplets, measured with sufficient accuracy in each case, sufficiently indicates that this mode of correcting the triplet separations in forming the ratio of squares of atomic weights cannot be valid. In fact, the two expressions on the left could only be equal if $\Delta\nu_2/\Delta\nu_2'$ were also equal $(\mathrm{Cd})^2/(\mathrm{Zn})^2$, and this is only approximately true for these two elements, and very far from true when mercury is taken as one of the elements. Some of the other lines taken to be homologous by Watts are certainly not corresponding lines, and it is difficult to understand on what principle they were selected. The deduced values for Zn range from 64·77 to 67·08.

### Separations and Atomic Numbers.

Since atomic numbers probably determine the places of the elements in the periodic table more correctly than the atomic weights, several attempts have been made to correlate these numbers with the series spectra.

In a graphical repetition of Runge and Precht's work on the doublet separations

in the calcium group Ives and Stuhlmann* found that the results were somewhat more consistent than for the atomic weights, but the atomic number derived for radium was 96, in place of the true value 88. Using the wave-number differences between extreme members of the triplets occurring in elements of the same group, it was found also by Anslow and Howell† that when the logarithms of these differences were plotted against the logarithms of the atomic numbers, the points fell more accurately on a straight line than with atomic weights, and an atomic number of 87 was deduced for radium.

Separations in relation to atomic numbers have also been discussed by H. Bell,‡ who employed two formulæ, namely :—

$$(1)\ \sqrt{\Delta\nu}=m(N-N_0)\ ; \qquad (2)\ \log \Delta\nu=p \log N+q$$

where $\Delta\nu$ is the separation, $N$ the atomic number, and the other terms are constants to be calculated for each group of elements. The figures for the alkali group will serve for illustration :—

| | At. No. | $\Delta\nu$ obs. | $\Delta\nu$ calc. (1). | $\Delta\nu$ calc. (2). |
|---|---|---|---|---|
| Li ... | 3 | 0·34§ | 0·25 | 1·03 |
| Na | 11 | 17·21 | 16·48 | 17·21 |
| K ... | 19 | 57·90 | 58·0 | 56·17 |
| Rb ... | 37 | 237·71 | 244·0 | 237·7 |
| Cs ... | 55 | 564·10 | 558·3 | 560·8 |

$m=0{\cdot}4447$ ; $N_0=1{\cdot}875$ ; $p=2{\cdot}1645$ ; $q=-1{\cdot}01832$.

A somewhat similar formula was tested by Paulson,‖ namely

$$\log \Delta\nu=A \log (N+n)+B$$

where $N$ is the atomic number, $\Delta\nu$ the separation, $A$ and $B$ constants, and $n$ a positive or negative integer. For each group of elements the value of $n$ was first determined graphically, and the constants $A$ and $B$ were then calculated by the method of least squares. The atomic numbers used were those of Rydberg's system,¶ which are two units higher than those of Moseley. The nature of Paulson's results may be gathered from the following data for the triplets of the calcium group :—

$$\log \Delta\nu_1=2{\cdot}163129 \log N-0{\cdot}871542$$
$$\log \Delta\nu_2=1{\cdot}748748 \log (N-4)-0{\cdot}459734$$

| | $N$. (Rydberg.) | $\Delta\nu_1$. | $\Delta\nu_2$. | $\Delta\nu_1$ calc. | $O-C$. | $\Delta\nu_2$ calc. | $O-C$. |
|---|---|---|---|---|---|---|---|
| Mg ... | 14 | 40·92 | 19·89 | 40·52 | +0·40 | 19·45 | +0·44 |
| Ca ... | 22 | 105·99 | 52·11 | 107·72 | —1·73 | 54·38 | —2·27 |
| Sr ... | 40 | 394·44 | 187·05 | 392·57 | +1·87 | 182·74 | +4·31 |
| Ba ... | 58 | 878·4 | 370·3 | 876·96 | +1·44 | 371·35 | —1·05 |
| Ra ... | 90 | — | — | (2268) | — | (838) | — |

The extrapolation to radium does not agree at all closely with the separations 2016·64 and 1036·15 afterwards suggested by Anslow and Howell. It will be observed

* Phys. Rev., **5**, 368 (1915).
† Loc. cit.
‡ Phil. Mag., (6) **36**, 337 (1918).
§ Not used in calculation of constants.
‖ Astrophys. Jour., **49**, 276 (1919).
¶ Jour. Ch. Phys., **12**, No. 5 (1914).

that no simple connection between the atomic numbers and the doublet or triplet separations has yet been discovered.

There does not appear to be any published record of investigations of the limits of series in relation to atomic numbers, but a few trials will show that the results are generally similar, and not more exact, than for the atomic weights. Thus, in the alkali group, potassium remains decidedly discordant, and in the calcium group, calcium again shows considerable departure from the approximate regularity shown by the other four elements. When the limits of the principal series are plotted against atomic numbers the points show the same absence of simple regularity which was found with the atomic weights.

## Conclusions.

These results are in a sense disappointing. It would seem that the spectra must for the present be regarded as constants of the elements which show no simpler relation to other constants than is shown by some of the constants among themselves. Thus, in the alkali group, the curve connecting atomic weights with melting points, or that connecting atomic weights and atomic volumes, is closely similar to that relating the limits of the subordinate series to atomic weights, and a similar discrepancy is shown by potassium in each case. Again, there is no simple relation between the atomic weights and densities in this group of elements, just as there is no simple law connecting the limits of the principal series. It can only be concluded that although the spectra change progressively with atomic weights, atomic volumes or atomic numbers, the laws governing the changes are not clearly indicated by any of the foregoing investigations.

# CHAPTER VIII.

## THE WORK OF HICKS.

The discussion of spectral series which has been made by Prof. W. M. Hicks* is of so special a character that it is most conveniently treated separately. The investigation covers a great deal of ground, and it will only be possible to attempt to give a general idea of some of the methods employed. In the earlier papers Hicks proves the value of the series formula

$$\nu = A - \frac{N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}$$

and makes a special feature of calculating the influence of possible errors of observation on the values of the constants for the different series. Having determined the constants for many of the known series, he proceeds to discuss them in relation to the atomic volumes and atomic weights of the respective elements. The adopted wave-lengths are on Rowland's scale, and as the conclusions would not be modified by the substitution of wave-lengths on the international scale, it has not been thought necessary to recompute the formula constants and the quantities which depend upon them.

It should be remarked that in some of his papers Hicks departs from the more usual practice, and writes, for example, p(1), instead of 1 p, for the variable part or " term " of the first principal line.

### Atomic Volumes.

Among the more striking results obtained by Hicks in his first paper is the following comparison of the constants for the stronger components of the principal series of the alkali metals with the atomic volumes. The limits of the series are also entered for completeness :

| | $\mu$ | $\alpha$ | $\mu-1$ | $\mu-1+\alpha$ | At. vol. | Limit. |
|---|---|---|---|---|---|---|
| Li ... | 0·951609 | +0·007365 | | | 1×11·81 | 43,486 |
| Na... | 1·148678 | —0·031776 | 2×0·074339 | 2×0·058451 | 2×11·80 | 41,449 |
| K ... | 1·296480 | —0·062511 | 4×0·074120 | 4×0·058492 | 4×11·15 | 35,006 |
| Rb... | 1·366399 | —0·074554 | 5×0·073280 | 5×0·058369 | 5×11·21 | 33,689 |
| Cs ... | 1·450967 | —0·090077 | 6×0·075161 | 6×0·060148 | 6×11·76 | 31,405 |

The constants $(\mu-1)$ and $(\mu-1+\alpha)$ are thus approximately integral multiples of constant numbers, and the atomic volumes the same multiples of another number. Lithium is excluded in this mode of treating the formula constants, and Hicks has suggested that what is usually regarded as the principal series of lithium may really be a combination $1s-md$ or $1s-mf$; the easy reversal of the lines, and the similarity to the principal series of the other alkali elements, however, is directly opposed to this supposition. Assuming the above relation to be sufficiently general, and observing that $\alpha/(\mu-1)$ is nearly constant, Hicks endeavoured to bring the figures into closer agreement by the introduction of an atomic weight term as a correction to $\mu$ (*I*.79).

* I., Phil. Trans., A. **210**, 57-111 (1910); II., **212**, 33-73 (1912); III., **213**, 323-420 (1914); IV., **217**, 361-410 (1917); V., **220**, 335-468 (1919). Corresponding numbers are used for references to these papers in the text.

### Atomic Weight Term.

The atomic weight term, as defined by Hicks, depends jointly upon the separations of doublets or triplets, and the limits of the subordinate series. Thus, if $D$ represents denominator, the formulae for the two members of a sharp series of doublets may be written:

$$\sigma_1(m)=N/D_1^2-N/D_m^2$$
$$\sigma_2(m)=N/(D_1-\Delta)^2-N/D_m^2$$

$\Delta$ is then the atomic weight term as represented in the later papers of Hicks, and is equivalent to the $2W$ of the first paper. In triplet series the two separations give $\Delta_1$ and $\Delta_2$, of which the former is the greater.

Hicks was led to conclude that there is a universal constant, approximately 0·21520, so that the denominator of the principal sequences of the alkalies, or of the sharp sequences in the elements of the second and third groups might be represented by

$$m+1-W\left(1-\frac{1}{m}\right)+a\left(1-\frac{k}{m}\right)sv$$

where $a$ and $k$ are constants for all elements, not very different from $0{\cdot}002740/(1-k)$ and 0·21520 respectively. $v$ is the atomic volume, and $s$ is an integer special to each element as follows:

| | | | |
|---|---|---|---|
| Na 2 | Mg 8 | Zn 9 | Al 8 |
| K 2 | Ca 7 | Cd 8 | Ga 8 |
| Rb 2 | Sr 6 | Hg 6 | In 6 |
| Cs 2 | | | Tl 5 |

If $k$ be taken$=0{\cdot}21520$, $a=0{\cdot}003490$. $W$ is to be taken as $\Delta/2$ for doublets, and as $\Delta_2$ for triplets.

In order to indicate the degree of approximation given by the general formula, the following comparison may be made with the values of the denominators calculated from the regular series formulæ:

| Element. | Series. | At. vol. | $s$ | $\Delta/2$ | $\Delta_2$ | True denominator. | From general formula. |
|---|---|---|---|---|---|---|---|
| K ... | $\pi_1$ | 44·60 | 2 | 0·001466 | | (1) 2·233969<br>(2) 3·265225 | 2·244315<br>3·277078 |
| Ca ... | $s_1$ | 25·5 | 7 | | 0·001368 | (1) 2·484198<br>(2) 3·522799 | 2·488903<br>3·555250 |
| Zn ... | $s_1$ | 9·33 | 9 | | 0·003475 | (1) 2·227899<br>(2) 3·257479 | 2·229991<br>3·259785 |

It will be seen that the correspondence is far from perfect, and after the exhaustive investigation made by Hicks it may be doubted whether it is really possible to deduce such a formula which shall be applicable to all elements. The atomic volume, given by atomic weight divided by density, as Hicks remarks, varies with temperature and cannot be directly involved in the spectral relations; it would seem, however, that it may be closely related to an atomic property analogous to volume, or sphere of action, on which the structure of the spectrum in part depends.

It should be particularly noted that the atomic volume term, according to Hicks, does not appear in connection with the diffuse and fundamental series; in the alkalies it is associated with the principal sequence, and in other groups of elements with the sharp sequence.

THE OUN.

Reference has already been made (p. 46) to the discussion by Ritz of the terms $(p_1-p_2)/W^2$, from which it appeared that the range of values was much less for all elements than in the case of $\Delta\nu/W^2$. Hicks (III.) has made a somewhat similar investigation, but has taken the whole denominator terms into account in forming the ratios. Taking $W$ as the atomic weight of an element, $w=W/100$, $\Delta$ the denominator difference which gives rise to the doublet separations, $\Delta_1$ and $\Delta_2$ the corresponding numbers for triplets, Hicks concludes that $\Delta$ is in all cases a multiple of $qw^2$, where $q$ has the same value for all elements (=about 90·5, when $\Delta$ is multiplied by $10^6$). The quantity $qw^2$ is that which Hicks has named the *oun* ($\omega\nu$), each element thus having an oun peculiar to itself and dependent upon the atomic weight. The oun is designated $\delta_1$, but the multiple $4\delta_1$ occurs most frequently and is indicated by $\delta$. We thus have:

$$\delta_1=qw^2=1 \text{ oun for element of atomic weight } 100w$$
$$\delta=4qw^2=4 \text{ ouns}$$
$$10^6\Delta=m\delta_1 \text{ or } m\delta, \text{ where } m \text{ is an integer special to each element.}$$

The derivation of the calcium oun may be taken for illustration. The triplet separations are 105·89 and 52·09. The limits of the sharp series are 33983·45, 34089·34, and 34141·43, and when these are put in the form $N/D^2$, the denominators ($D$) are 1·796470, 1·793679, 1·792310. The denominator differences are therefore $\Delta_1=0{\cdot}002791$, $\Delta_2=0{\cdot}001369$, which are multiplied by $10^6$ and tabulated as 2,791 and 1,369. The atomic weight is taken to be 40·124, so that $10^6\Delta_1/w^2=17336{\cdot}1=48\times361{\cdot}169$, where the last factor is the number nearest to $4q$ which makes the multiplier an integer. The value of $\delta$ for calcium is thus $361{\cdot}169\times(0{\cdot}40124)^2=58{\cdot}14$; or $\delta=10^6\Delta_1/48=58{\cdot}14$.

This process has been applied by Hicks to a large number of series, and some of the results are given in the following table:

| | $\sigma_1\infty$ | $W=100w$ | $\Delta\nu$ (Sepn.) | $10^6\Delta$ | $10^6\Delta/w^2$ | $mq$ or $m.4q$ | $\delta=4qw^2$ $=4$ ouns | $361{\cdot}8\pm$ |
|---|---|---|---|---|---|---|---|---|
| Na | 24475·40 | 22·998 | 17·175 | 743 | 14027·96 | 155× 90·50 | 19·17 | 0·2, 0·14 |
| K | 21964·44 | 39·097 | 57·87 | 2,939 | 19224·86 | 53×362·72 | 55·45 | 0·92, 3·22 |
| Rb | 20871·29 | 85·448 | 237·54 | 12,935 | 17715·86 | 49×361·40 | 263·77 | —0·40, 0·56 |
| Cs | 19673·00 | 132·823 | 553·80 | 32,551 | 18449·48 | 51×361·74 | 638·22 | —0·06, 0·33 |

The last column gives the difference between 361·8 and the number under $4q$, except that when it is not the $4\times90{\cdot}5$ term it is brought up to it by multiplying by 4. The second set of figures in this column shows the limits of permissible variation of the deduced $4q$, due to uncertainties in the measures of the lines. In nearly all cases the differences from 361·8 are within the possible errors depending upon imperfect data.

In this way, Hicks found from 17 elements, weighted according to the possible errors:

$$1 \text{ oun}=\delta_1=(90{\cdot}4725\pm0{\cdot}013)w^2$$
$$4 \text{ ouns}=\delta=361{\cdot}89w^2$$

The oun, according to Hicks, appears in connection with series in several other ways. The satellite separations, for example, are dependent upon multiples of the oun, and in the case of triplets $\Delta_1-2\Delta_2$ is also an oun multiple.

It should be observed that formulae for series do not enter into this discussion, except as regards the adopted value of $N$ and the determination of limits. Except when the oun is very small, Hicks believes that with the accuracy now attainable in spectroscopic observations, it should be possible to obtain far more reliable values of the ouns of the various elements, and thence of the atomic weights, than by processes depending upon weighing. There is, however, usually no apparent regularity in the multiplying integers which determine the doublet or triplet separations, even among elements of the same group, so that the simplest application of the spectroscopic method is to assume an approximate atomic weight in order to evaluate the multiple, and then to use this to correct the atomic weight.

By this method Hicks has since made determinations of the atomic weights of copper and gold, taking silver as standard with atomic weight 107·88.* The results may be summarised as follows :—

| | Doublet separation ($\Delta\nu$) | $\sigma_{1\infty}$ | $10^6\Delta$ | $\delta$ | Multiple of $\delta$ | $W=100\sqrt{\delta/4q}$ |
|---|---|---|---|---|---|---|
| Cu ..... | 248·44 | 31523·48 | 7307·087 | 146·1419 | 50 | 63·5569 ± ·006 |
| Ag ..... | 920·438 | 30644·60 | 27786·57 | 421·047 | 66 | 107·88(assumed) |
| Au ..... | 3815·56 | 29469·85 | 113951·00 | 1406·802 | 81 | 197·193 ± ·003 |

The value of the constant $4q$ deduced from Ag is 361·7837 ± ·0038, and this was used in calculating the atomic weights of Cu and Au from the $\delta$ terms. Brauner's values are 63·56 ± ·01, 197·20 ± ·07 respectively for these elements. It should be observed that the separations of the pairs of lines involved in these determinations can be measured with great accuracy, but that the exact determination of the limits of the series is less certain.

In some cases the spectroscopic determination may be made independently of any previous knowledge of the atomic weight, by utilising the various different ways in which the oun is considered to play a part in building up the spectrum, and finding the smallest common factor. An illustration is given later (p. 58).

## Collaterals.

Further evidence of the oun as a controlling influence on the spectrum is adduced by Hicks from the supposed existence of what he has called "collaterals." In the case of doublets and triplets, the second, or second and third components may be considered as having received a sort of lateral displacement by the atomic weight term $\Delta$, or $\Delta_1$ and $\Delta_2$, and may thus be regarded as collaterals of the first. Hicks believes that this kind of displacement is not restricted to doublets and triplets, or their satellites, but is of very common occurrence. Thus, if the wave-number of a series line be $N/D_1^2 - N/D_m^2$, lateral displacements may be produced by the addition or subtraction of multiples of $\delta$ or $\Delta$, say $x\delta$ or $x\Delta$, to $D_1$ or $D_m$. When added to $D_1$ the operation is indicated by writing $x\delta$ to the left of the symbol of the original line, and when added to $D_m$ to the right. As an illustration, Hicks takes the Ca line at $\lambda$ 6439·36. This may be represented by $(2\Delta_1+10\Delta_2)$ Ca $s_1(2)(+\Delta_2)$, meaning that whereas

$$\text{Wave No. of Ca } s_1(2) = \frac{N}{(1{\cdot}796470)^2} - \frac{N}{(2{\cdot}484994)^2}$$

* Phil. Mag., **38**, 6 & 301 ; **39**, 457.

$$\text{Wave No. of Ca } 6439{\cdot}36 = \frac{N}{(1{\cdot}796470+2\Delta_1+10\Delta_2)^2} - \frac{N}{(2{\cdot}484994+\Delta_2)^2}$$

$$= \frac{N}{(1{\cdot}815732)^2} - \frac{N}{(2{\cdot}486362)^2}$$

$$(10^6)\Delta_1 = 2791\ ;\ (10^6)\Delta_2 = 1369.$$

In this way Hicks accounts for irregularities in the satellite separations which sometimes occur, and for discrepancies between the observed positions of certain lines and the positions calculated from formulae. In some cases he considers that the whole set of lines for a given order number $m$ may be replaced by another strong set displaced by several multiples of $\Delta$, or by a congeries of fainter lines displaced by various oun multiples.

The whole procedure, however, seems to be somewhat arbitrary, and it remains to be seen how it will bear the test when observations of sufficient accuracy for such a purpose become available. Some of the examples first mentioned by Hicks are certainly no longer admissible ; Mg $d_1(4)$, for instance (III., 356), has since been shown to be perfectly normal by the resolution of the line into two components.*

## Constitution of Diffuse Series.

Hicks has further concluded that the diffuse and fundamental series cannot be represented by a continuous mathematical expression, though they may approximate to values so represented. He considers it more probable that they depend on discrete changes which are connected with the oun, or atomic weight term, in a way which has yet to be discovered. Thus, successive denominators ($D$) of a diffuse sequence are thought to differ by integral multiples of the oun. When there are no satellites, the denominators change by multiples of $\Delta$ in the case of doublets, and of $\Delta_2$ in the case of triplets, except that in the oxygen group the multiples are of $\Delta_1$. When satellites are present, the multiples are of $\delta$ or $\delta_1$. In addition, the decimal part, or mantissa, of the denominator of the normal first line of the diffuse series is itself a multiple of $\Delta$, the outer satellite being taken as the normal line. The general character of this part of the investigation will be sufficiently indicated by the first chief line and satellite of the diffuse series of caesium :—

$$\text{Cs } (10^6)\Delta = 32551,\quad (10^6)\delta = 638{\cdot}22,\quad D\infty = 19673{\cdot}0.$$

| Chief line. | | Satellite. |
|---|---|---|
| $2{\cdot}554329(228)-76\xi-43$ | $46\delta_1$ | $2{\cdot}546989(226)-97$ |
| $30\delta$ | | |
| $3{\cdot}535183(200)-201\xi+40$ | $54\delta_1$ | $3{\cdot}526567(200)+9$ |
| $10\delta_1$ | | |
| $4{\cdot}533588(160)-424\xi+1$ | $14\delta$ | $4{\cdot}524635-161$ |
| $3\delta_1$ | | |
| $5{\cdot}533110(400)-768\xi+22$ | $14\delta$ | $5{\cdot}524175-26$ |
| &c. | | |

$$546989 = 857(638{\cdot}260 \pm 0{\cdot}233 - 0{\cdot}0887\xi) = 857\delta$$

In this table the denominator terms have been adjusted within permissible limits indicated by the possible errors of observation. The number in brackets following the denominator term is the estimated limit of error in the last three digits, $\xi$ is the error of the limit, and the last number represents the difference

* Fowler & Reynolds, Proc. Roy. Soc., A. **89**, 139 (1913).

between the observed value of the denominator and the "selected" value entered in the table. The multiples of $\delta$ or $\delta_1$ in the middle of the table are the satellite separations, expressed in terms of denominator differences.

It is extremely difficult to form a just estimate of the confidence which may be placed in these results, on account of uncertainties in many of the observational data, and the occasional exceptions to the more general rules above stated. Thus Cs is exceptional inasmuch as the first mantissa is a multiple of $\delta$ and not of $\Delta$; and Cd is irregular because it is the mantissa of the chief line, and not that of the outer satellite, which is a multiple of $\Delta$. Very few spectra have been measured with the accuracy and completeness which would seem to be necessary to justify the deductions fully, and the adjustment of data within estimated permissible ranges is not an entirely satisfactory substitute. The apparent absence of any general law governing the sequence of multiplying integers in the successive denominator terms is somewhat disappointing, for it is clear that the oun theory does not yet provide a guide to the identification of series lines such as is provided even by an approximate formula.

## Links.

In his fourth paper, Hicks has extended the idea of collateral displacements with a view to associating the lines which do not fall into the ordinary series with those which belong to the regular series systems. Each line of a series is regarded as being connected with other lines in the same spectrum through several constant differences of wave-number, or *links*, which may be added or subtracted to an indefinite extent, and apparently in any order. The various links which occur in a doublet system are distinguished by letters which have the following meanings, as given by Hicks, and as written in the more extended notation of this report :—

$$\begin{aligned}
a&=p-p(\Delta) &&=N/(1+p_1)^2-N/(1+p_1+\Delta)^2\\
b&=p(-\Delta)-p &&=N/(1+p_1-\Delta)^2-N/(1+p_1)^2\\
c&=p(-2\Delta)-p(-\Delta) &&=N/(1+p_1-2\Delta)^2-N/(1+p_1-\Delta)^2\\
d&=p(-3\Delta)-p(-2\Delta) &&=N/(1+p_1-3\Delta)^2-N/(1+p_1-2\Delta)^2\\
e&=p(-3\Delta)-p(\Delta) &&=N/(1+p_1-3\Delta)^2-N/(1+p_1+\Delta)^2\\
u&=s-s(\Delta) &&=N/(1+s)^2-N/(1+s+\Delta)^2\\
v&=s(-\Delta)-s &&=N/(1+s-\Delta)^2-N/(1+s)^2.
\end{aligned}$$

As before, $\Delta$ is the denominator difference corresponding with the normal doublet separation. The link $b$ is the normal doublet separation, and link $e=a+b+c+d$.

These methods were first applied to the spark spectra of silver and gold, containing 600 and 741 lines respectively in the region covered by the investigation. It will suffice to take silver as an illustration :—

| Ag. | | Links. | Corrections to links. |
|---|---|---|---|
| $p=\sigma_1\infty$ | $=30644{\cdot}60$ | $a=880{\cdot}77$ | $a'-a=-0{\cdot}61x$ |
| | $=N/(1{\cdot}891807)^2$ | $b=920{\cdot}44$ | $b'-b=-0{\cdot}61x$ |
| $s=\pi\infty$ | $=61116{\cdot}33$ | $c=962{\cdot}54$ | $c'-c=-0{\cdot}66x$ |
| | $=N/(1{\cdot}339600)^2$ | $d=1007{\cdot}26$ | $d'-d=-0{\cdot}71x$ |
| $\Delta\nu$ (sepn.) | $=920{\cdot}435$ | $e=3771{\cdot}00$ | $e'-e=-2{\cdot}59x$ |
| $10^6\Delta$ | $=27786{\cdot}57$ | $u=2458{\cdot}64$ | $u'-u=-2{\cdot}25x$ |
| $\delta=10^6\Delta/66=$ | $421{\cdot}0087$ | $v=2616{\cdot}61$ | $v'-v=-2{\cdot}47x$ |

The links are, of course, in ordinary wave-number units.

It is further suggested that the links may be varied by making them depend on

displacement operations on values of $p$ and $s$ which have already been displaced by small multiples ($x$) of $\delta$ or $\delta_1$; thus, $a'=p(x\delta)-p(x\delta+\Delta)$; $b'=p(x\delta-\Delta)-p(x\delta)$, and so on. The calculated changes of the links are then as shown under $a'-a$, &c.

It will be seen that in a complex spectrum, with seven links and these permissible variations in each of them, there is room for many accidental coincidences, but the discussion of probabilities has convinced Hicks that the existence of the links, in the main, cannot be due to chance.

The following (IV., 366) are among the numerous suggested links occurring in silver, the differences in wave-numbers of the lines being enclosed in brackets, and decimal parts of the wave-numbers of the lines being omitted :—

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (1) | 30514 | (2460·39) | 32974 | (2460·84) | 35435 | (2461·00) | 37896 | (2457·26) | 40353 |
| (2) | 17814 | (3777·32) | 21591 | (3779·86) | 25371 | (3778·01) | 29149 | (3778·56) | 32928 |
| (3) | 30959 | (3776·44) | 34735 | (3777·47) | 38513 | (3773·79) | 42286 | (2618·00) | 44904 |

Hicks attaches great importance to these long series of the same links, as proving the reality of variations in the links. Thus, the differences in the second row are regarded as representing a modified link of about 3778·44 as compared with the calculated $e=3771{\cdot}00$. The normal $e$ link is thus changed to $e(-3\delta)$; that is, $[3771{\cdot}00+(3\times 2{\cdot}59)]$ with an outstanding error of 0·33. The link to another line, $P_1(1)$ at 30471 is $-2456{\cdot}59$, which is equivalent to $u(\delta)+0{\cdot}20$.

Proceeding in this way, Hicks has drawn up extensive tables and maps which are intended to show that a great number of lines may be connected with ordinary series lines by links and chains, but most of them are too complex for reproduction. As giving some indication of the nature of the results, however, the short linkage starting from Ag $\sigma_1(4)$, ($\lambda 3981{\cdot}87$; $\nu=25106{\cdot}89$) may be mentioned. The following are the observed wave-numbers and intervals between the successive lines :—

| | $\nu$ | $\Delta\nu$ |
|---|---|---|
| $\sigma_1(4)$ | 25106 | |
| | | 918·71 |
| $\sigma_2(4)$ | 26025 | |
| | | 3777·54 |
| | 29803 | |
| | | 919·58 |
| | 30722 | |
| | | −2619·34 |
| | 28103 | |

It may be deduced from Hicks's table (IV., 394) that these intervals are identified with links and modified links, such that

$$\begin{aligned}28103&=25106{\cdot}89+b+e(-2\delta)+b(2\delta)-v(-\delta)\\&=25106{\cdot}89+920{\cdot}44+(3771{\cdot}00+5{\cdot}18)+(920{\cdot}44-1{\cdot}22)\\&\qquad-(2616{\cdot}61+2{\cdot}47)\\&=28103{\cdot}65\end{aligned}$$

The observed $\nu$ is 28103·33 so that a correction of only −0·32, or of $\Delta\lambda=+{\cdot}025$, is required to make the sum of the links exact. $\sigma_2(4)$ is not a good observation and the assumption of the normal separation from $\sigma_1(4)$ is therefore permissible.

Some of the linkage systems which have been traced out in this manner are of great complexity; that starting from Ag $\pi_2(1)$, for example, involves more than 280 lines.

To what extent such results represent reality is not as yet very clear. Since

the numerical values of the various links have been determined from series of arc lines, it would scarcely be expected that they would be applicable also to spark lines, which, in all known spectra of this class, form independent series if series are recognisable at all.

### Summation Series.

An entirely novel idea has been introduced by Hicks in the suggestion that summation as well as difference series may occur in spectra. (V. 343.) That is, if there be an ordinary series $A-\varphi(m)$, there may also be a series $A+\varphi(m)$. In such cases the mean of two corresponding wave-numbers would obviously give the limit of the series very exactly.

Series believed to be of this type were first noted by Hicks in association with supposed fundamental series of the rare gases, and others were afterwards suggested in connection with series of other types.* In general, the limits of the $P$, $S$, and $D$ series are far larger than $F\infty$, so that associated summation series would most frequently lie beyond the range of observation. Hicks considers that the existence of summation series is fully established by his investigations, but the evidence so far put forward is far from convincing. It is frequently necessary to introduce hypothetical displacements of unobserved lines which are out of range, and there is no apparent regularity in the intensities of the lines in the same set. It would, therefore, not be possible to recognise any of the suggested summation series as such by ordinary inspection of photographs, or by any independent procedure. Moreover, it is remarkable that none of the well-established series having limits less than, say wave-number 26,000 are repeated in inverse order in the ordinary range of observations in the ultra-violet.

### Independent Determination of Atomic Weight.

As a further example of the possible use of the oun, the determination of the atomic weight of an element, without assuming any knowledge from chemical operations, may be mentioned. The procedure may be illustrated by the spectrum of zinc,† for which $(10^6)\ \Delta_1=7204$, and $(10^6)\ \Delta_2=3486$.

We have $\Delta_1-2\Delta_2=232$, which may be a small multiple of $\delta_1$, especially as $\Delta_1$ and $\Delta_2$ are nearly exact multiples of 232.

The satellites to $D(2)$ give denominator differences of 581 and 348; the difference is again nearly 232, but this cannot be the oun because 581 and 348 are not multiples of 232. The satellites to $D(3)$ give denominator differences of 504 and 388, which differ by 116, or half of 232. But 116 cannot be the oun because, although it divides 581 and 348, it does not divide 504 and 388. The half of 116 fails to satisfy the imposed conditions, but one-third of 116, or 38·7, divides all the numbers given above. No smaller number than this is required in any connection, and 38·7 is therefore the small oun of zinc, $\delta_1$.

$\Delta_1$ should be an exact multiple of $\delta_1$, in this case 186 $\delta_1$, and so a more correct value of $\delta_1$ is given by $7204/186=38{\cdot}731$, or $\delta=154{\cdot}92$.

The atomic weight is then $\sqrt{(154{\cdot}92\times100^2)\div361{\cdot}89}=65{\cdot}43$.

The example is merely by way of illustration, since the "adjusted" figures given by Hicks (III, 346) have been used. As already remarked, it would be simpler to assume the chemical determination of the atomic weight, and to use the spectroscopic data merely as a means of correcting the assumed value.

* Phil. Mag., **38**, 6, and 301 (1919); **39**, 457 (1920).

† The author is indebted to Prof. Hicks for this example.

# CHAPTER IX.

## APPLICATIONS OF BOHR'S THEORY.

It is not the purpose of the present Report to present an account of theories of the origin of spectra, but Bohr's theory* calls for some mention because of the simplified view which it gives of the structure of the spectra themselves.

Our first idea as to the origin of spectral lines might very well have been that a line is produced by the revolution of an electron about a centre, and that the frequency of the line would correspond with the frequency of revolution in the orbit. The analysis of spectra, however, has shown that the frequency of a line always appears as the difference of two "terms," neither of which represents a spectral line, though one may represent the limit of a series. Hence, a complete theory must in the first place give a physical meaning to these terms, and in the second place explain how an emitted frequency comes to be the difference of two of them.

Bohr adopts the "nucleus atom" theory of Rutherford, which supposes an atom to consist of a positively charged nucleus and a system of external electrons such that in the neutral atom the total negative charge of the electrons is equal to the positive charge of the nucleus.† On this basis, with the aid of the quantum theory of radiation, Bohr has developed a theory of spectra which leads to formulæ for the spectra of hydrogen and ionised helium, and represents these spectra quantitatively. The theory also gives a general indication of the structure of other spectra, but the difficulties involved in their calculation have not yet been overcome.

A summary of the theory has already been given by Jeans in his report on "Radiation and the Quantum Theory,"‡ and later developments have been reviewed by Silberstein in a report on "The Quantum Theory of Spectra."§ Important extensions of the theory to the explanation of the "fine structure" of the lines of hydrogen and ionised helium have been made by Sommerfeld.||

### The Spectrum of Hydrogen.

In the case of hydrogen, the atom consists of a nucleus having unit + charge, and a single electron in orbital motion around it. The circumstances of this motion may be calculated from the ordinary laws of mechanics, but the electron is supposed only to be free to traverse certain specified orbits, which are determined in the case of circular orbits by the condition that the angular momentum is an integral multiple of $h/2\pi$, where $h$ is Planck's constant of action. When the electron moves in one of these "stationary" orbits there is no radiation, and emission occurs only when the electron passes from one stationary orbit to another. Without attempting to indicate the mechanism of the passage from orbit to orbit, Bohr supposes that the transition is followed by the emission of a homogeneous radiation, the frequency of

* Phil. Mag., **26**, 1,476 (1913). Dan. Acad. Sc., IV., 1, Parts I. & II., pp. 1-100 (1918).

† The nucleus itself is probably of complex structure, including hydrogen nuclei and electrons, and its effective charge is the "residual" charge, corresponding to the atomic number of the element.—Rutherford, Proc. Roy. Soc., A. **97**, 374 (1920).

‡ Phys. Soc. (1914).

§ London: Adam Hilger (1920).

|| Atombau und Spektrallinien, 2nd edition, p. 306 (Braunschweig, 1921).

which can be determined from the quantum theory. The energy radiated is equal to the difference of the energies of the electron in the two orbits concerned, and is assumed to be one quantum of magnitude $\varepsilon = hn$, where $n$ is the frequency. At any instant, a single atom contributes to only one line of the spectrum, and it is the summation of the radiations from a large number of atoms that accounts for the whole series of lines.

Taking $E$ and $M$ as the charge and mass of the nucleus, $e$ and $m$ as the charge and mass of the electron, the theoretical formula for the hydrogen spectrum, in a first approximation, is

$$\nu = \frac{2\pi^2 E^2 e^2}{ch^3} \cdot m\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

where $\tau_1$ and $\tau_2$ are integers, $c$ is the velocity of light, and $\nu(=n/c)$ gives the wave-numbers of the lines.

When the mass of the electron is not considered negligible in comparison with that of the nucleus, and since $E=e$ in the case of hydrogen, the formula becomes

$$\nu = \frac{2\pi^2 e^4}{ch^3} \cdot \frac{Mm}{M+m}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

The formula is thus of precisely the same form as that which has been found to represent the spectrum of hydrogen (p. 14), the expression outside the bracket representing the Rydberg constant. The correspondence is not merely qualitative, as would be expected from the assumptions which have been made, but the theoretical agrees with the observed value within the limits of experimental errors.*

When $\tau_1=2$ and $\tau_2=3, 4, 5 \ldots$ the formula represents the Balmer series; if $\tau_1=1$, $\tau_2=2, 3 \ldots$ we get the far ultra-violet series observed by Lyman, and if $\tau_1=3$ we get the infra-red series partially observed by Paschen.

The radii of the stationary orbits vary as the squares of the integers $\tau$, the theoretical values being given by

$$a = \frac{\tau^2 h^2}{4\pi^2 e^2 m}$$

The successive orbits may thus be represented as in Fig. 9 by drawing circles with radii $1^2, 2^2, 3^2 \ldots$ In the normal state of the atom, the electron revolves in the innermost orbit. When the atom is disturbed, as by the electric discharge in a vacuum tube, so that the electron is removed to a great distance from the nucleus, the electron will generally occupy successively different orbits on its return. The first line of Lyman's ultra-violet series corresponds to the fall of the electron from orbit 2 to orbit 1, the second line to the fall from orbit 3 to orbit 1, and so on. Similarly, the lines of the Balmer series are produced by falls from orbits 3, 4, 5 . . . to orbit 2; and the lines of the infra-red series by falls from orbits 4, 5 . . . to orbit 3.

* Using Millikan's data ("The Electron," p. 210), $e=4{\cdot}774\times10^{-10}$, $h=6{\cdot}545\times10^{-27}$, $e/m=1{\cdot}767\times10^{7}$, the theoretical value of $N$, in terms of oscillation frequency, is $3{\cdot}294\times10^{15}$, as compared with the spectroscopic value $3{\cdot}290\times10^{15}$. The substitution is conveniently made in the equation

$$N = \frac{2\pi^2 e^5}{h^3 e/m}$$

On this view, the line spectrum of hydrogen should include no lines other than those represented by the general formula

$$\nu = N\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

There is no place for any of the lines observed in stars by Pickering, or calculated by Rydberg, which were formerly attributed to hydrogen. This conclusion, it may be stated at once, is in complete accordance with our present experimental evidence.

The series of lines discovered by Pickering in the star $\zeta$ Puppis appeared to converge to the same limit as the Balmer series of hydrogen, and to be closely represented by substituting $(\tau_2+0{\cdot}5)$ for $\tau_2$ in the Balmer formula. This relation would be appropriate to the diffuse and sharp series of the same element, and thus

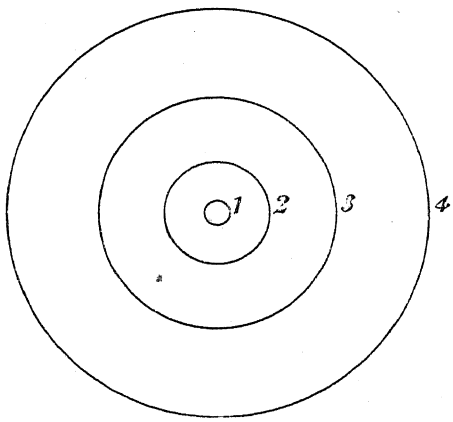


FIG. 9.—THE BOHR ORBITS FOR HYDROGEN.

suggested that the Pickering lines were due to a form of hydrogen which could not be produced in the laboratory, but might be supposed to exist in stars at very high temperatures. Adopting this view, Rydberg calculated the lines of the associated principal series, in accordance with the relations found for other elements, from the formula

$$\nu = N\left(\frac{1}{1{\cdot}5^2} - \frac{1}{\tau_2^2}\right)$$

The first "principal" line, given by $\tau_2=2$, would thus be at $\lambda$4,688, the second at $\lambda$2,734, and so on. All but the first lie beyond the region of atmospheric transparency, but the actual occurrence of a prominent line near 4,688 in $\zeta$ Puppis, as well as in many Wolf-Rayet stars and gaseous nebulæ, seemed to give strong support to Rydberg's theory, and the existence of a modified form of hydrogen was widely accepted. Lockyer designated it "proto-hydrogen," in the belief that it represented one of the final stages of simplification of matter by the action of high temperatures; it was also sometimes called "cosmic hydrogen."

Lines corresponding closely with this hypothetical spectrum were eventually obtained by Fowler* in experiments on helium in which hydrogen was present as

* Monthly Notices R.A.S., **73**, 62 (1912). Phil. Trans., A. **214**, 254 (1914).

an impurity. The wave-length of the supposed first principal line as determined in the laboratory was slightly lower than that calculated by Rydberg, viz., 4,685·98 on Rowland's scale, but was at first supposed to be in sufficient agreement. In addition to the lines 4,688, 2,734, &c., predicted by Rydberg, however, an intermediate series was found, with lines at λ3,203, &c., which was provisionally regarded as a second principal series, since its limit was identical with that of the "4,686" series. Three of the Pickering lines were also produced, their wave-lengths being approximately 5,411, 4,541, 4,200. In accordance with Rydberg's theory, these also were at first attributed to hydrogen, for they seemed to have a close numerical connection with the Balmer series, and no relation whatever to the known lines of helium.

The view that the lines in question were due to hydrogen, however, was not entirely satisfactory, partly because they could not be produced from hydrogen alone, and partly because the occurrence of lines not predicted by Rydberg broke the analogy with the series of other elements. Fowler sought to estimate the value of the numerical evidence on which the identification with hydrogen mainly depended by a search for other examples of series of the "second principal" type, but the whole question was satisfactorily settled by Bohr in the extension of his theory to ionised helium.

### Ionised Helium ($He^+$).

There is good reason to believe that the helium atom consists of a doubly-charged nucleus of four times the mass of the hydrogen nucleus, with two electrons revolving round it. When the gas is subjected to discharges of moderate intensity, one of the electrons may be supposed to be displaced, and the ordinary spectrum of helium to be emitted when this moves to different orbits on its return; the theory of this spectrum, however, is not yet complete. Under the action of sufficiently strong excitation, both electrons are supposed to be removed from the normal orbit, and a second totally different spectrum to be emitted when only one of them returns. The formula for the series of lines developed will be identical in a first approximation with that for hydrogen, except that $E$ is now to be replaced by $2e$; thus

$$\nu=\frac{8\pi^2e^4m}{ch^3}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=4N\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

When the mass of the electron is taken into account

$$\nu=\frac{8\pi^2e^4}{ch^3}\cdot\frac{M'm}{M'+m}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=4N'\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

where $M'=4M$, and $N'$ differs slightly from $N$.

When $\tau_1$ is put $=3$ in the approximate formula, the substitution of 4, 6, 8 . . . for $\tau_2$ will obviously give lines identical in position with those calculated for the supposed principal series of hydrogen by Rydberg, while $\tau_2=5$, 7, 9, will give lines nearly coincident with the "second principal" series of hydrogen observed by Fowler. Bohr's theory, however, unites both in a single series of a new type, and assigns them to ionised helium. The small deviations of the observed lines from Rydberg's calculated values are accurately accounted for by the difference between $N$ and $N'$, depending upon the difference of atomic weights.

As to the Pickering lines, Bohr's theory indicated that associated with these in a single series there ought to be lines nearly coincident with the Balmer series of

hydrogen, the Pickering lines being given by $\tau_1=4$, $\tau_2=7, 9, 11\ldots$, and the additional lines by $\tau_2=6, 8, 10 \ldots$ The observation of some of the additional lines by Evans* and subsequently by Paschen,† together with the observations of the lines in the absence of all traces of hydrogen, gave additional support to the theory which attributes them to ionised helium.

The Pickering series, as thus extended, is compared with the Balmer series in Fig. 10. The difference in position of the lines at $H_\alpha$ is $2{\cdot}6A$, diminishing to $1{\cdot}6A$ at $H_\epsilon$. Expressed numerically, the formulæ for H and $He^+$ are respectively

$$\nu=109678{\cdot}3\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

$$\nu=(4\times109723{\cdot}22)\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right).$$

The ratio $\frac{N_{He^+}}{N_H}$ as thus determined from Fowler's observations is 4·001638.

The theoretical ratio is $\frac{4M_{He}(M_H+m)}{M_H(M_{He}+m)}$, and taking $M_H/m=1845$ in accordance with Millikan's experimental result, the numerical value is 4·001626, in close accordance with the observed ratio.

Conversely, the observed ratio may be utilised to derive the mass of the electron in terms of that of the hydrogen nucleus, giving $M_H/m=1831$.‡

Paschen§ has made a further investigation of the spectral constants, with relativity corrections and other refinements, and has obtained $M_H/m=1843{\cdot}7$.

There is now ample evidence both theoretical and experimental, that Rydberg's

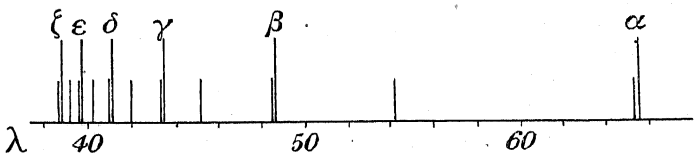


FIG. 10.—COMPARISON OF EXTENDED PICKERING SERIES WITH BALMER SERIES OF HYDROGEN.

hypothetical lines of hydrogen have no existence, and that the lines observed in stars and in the laboratory near their positions are really the enhanced lines due to ionised helium. Further support for this conclusion is afforded by Fowler's demonstration that enhanced lines of other elements also have $4N$ for the series constant.

It will be observed that on Bohr's theory the Balmer and associated series represent the final simplification of the hydrogen spectrum, and that the "4686" and associated series similarly represent the simplest possible spectrum of helium. In other elements, however, it is conceivable that further simplifications may occur, corresponding to the loss of two or more electrons and giving rise to series having $9N$, or still higher multiples, for the series constant. The existence of such series

*Phil. Mag., **29**, 284 (1915).

†Ann. d. Phys., **50**, 901 (1916).

‡Fowler's original value, when the measures were expressed on Rowland's scale, was $1836\pm12$.

§ Loc. cit.

has not yet been completely demonstrated. On account of the high value of the series constant, the strongest lines of this class will probably lie in the extreme ultra-violet.

### Arc Spectra.

The theory has not yet been developed so as to give a complete representation of the spectra of elements other than hydrogen and ionised helium. In neutral helium, which is the next in order of simplicity of atomic structure, the ordinary spectrum arises from the interaction of a displaced electron with a system consisting of the nucleus and the other electron. The residual charge of the central system is thus one unit, as in hydrogen, and the force on the electron, when at a great distance from the nucleus, will be nearly the same as in the hydrogen atom. The series constant for the spectrum of the neutral atoms will therefore be nearly the same as that for hydrogen. The detailed discussion of the possible stationary orbits indicated by the actual spectrum, however, is very complicated.

A similar consideration of the spectra of elements in which the atoms include a larger number of electrons suggests an explanation of the appearance of the Rydberg constant in the formulae for series of other elements.

The series constant may be expected to show a small variation with the atomic weight of the element, as already indicated in the case of helium. Thus, if $M$ be the mass of the atomic nucleus, and $m$ that of the electron, the Rydberg constant for hydrogen is of the form

$$N_H = k\frac{Mm}{M+m}$$

For any other element of atomic weight $A$ in terms of hydrogen,

$$N_A = k\frac{AMm}{AM+m}$$

and we have the ratio

$$\frac{N_A}{N_H} = \frac{A(M+m)}{AM+m} = \frac{M/m+1}{M/m+1/A}$$

Taking Millikan's value for hydrogen $M/m=1845$, we get

$$\frac{N_A}{N_H} = \frac{1846}{1845+1/A}$$

With Curtis's value 109678·3 for $N_H$, we thus find $N_{He}=109722{\cdot}9$, $N_{Li}=109729{\cdot}25$, and $N_\infty=109737{\cdot}7$.*

It is only in connection with hydrogen and ionised helium, however, that the precise value of $N$ is at present of importance. With the approximate series formulae adapted to other spectra, the hydrogen constant may be used without disadvantage in ordinary calculations.

### Spark Spectra.

The series of enhanced lines which are especially developed in spark spectra, as first clearly shown by Fowler† for Mg, Ca, and Sr, are characterised by the appearance of the series constant with four times its ordinary value. Such series,

* In a discussion of data relating to the fine structure of the lines, R. T. Birge has deduced the value $109677{\cdot}7 \pm 0{\cdot}2$ for hydrogen, and $109736{\cdot}9 \pm 0{\cdot}2$ for a nucleus with infinite mass. Phys. Rev., **17**, 589 (May, 1921).

† Bakerian Lecture. Phil. Trans., A. **214**, 225 (1914).

as in ionised helium, are therefore to be attributed to the ionised elements; that is, two electrons are to be supposed removed by the exciting source, and the enhanced series to be produced when one of them returns, the central system then having a net charge of two units. When the second electron returns its interaction is with a central system having only one unit charge, and the ordinary arc series are developed; the atom as a whole is then neutral. The two spectra are as different as if they belonged to two different elements, and since the systems producing them cannot co-exist, there are no lines arising from combinations of the terms of the arc and spark series.

As a general conclusion from Bohr's theory, it would thus appear that all series having $N$ for the series constant are produced by neutral atoms, while those having $4N$ for the constant have their origin in ionised atoms. If three electrons were removed by the exciting source, the return of one of them while two remained detached would be marked by the appearance of series having $9N$ for the series constant, and so on.

It should be observed that the energy necessary to produce the enhanced lines varies from element to element. In Ca, Sr, Ba, for example, these lines are strongly developed even in the ordinary arc, though they are relatively much strengthened in the spark (*see* Plate IV.). In many elements, including the alkali metals, on the other hand, such lines do not appear at all under the stimulus of the arc.

A possible connection between the limits of the principal series of enhanced lines and the limits of the principal series of singlets in the arc spectra of the elements of Group II. has been noted by E. Fues;* namely, that the former are about double the latter. He gives the following data in illustration:—

| | Mg | Ca | Sr | Zn | Cd |
|---|---|---|---|---|---|
| $P\infty$ (=1·5$S$) ... | 61,660 | 49,300 | 45,900 | 75,760 | 72,540 |
| $\pi\infty$ (=1·5$\sigma$) ... | 121,270 | 95,700 | 88,850 | 159,000 | 151,000 |
| $\frac{1\cdot5S}{1\cdot5\sigma}$ ... | 0·509 | 0·515 | 0·518 | 0·477 | 0·480 |

The ratios for Zn and Cd, with the limits shown in the tables which follow (147,544 and 140,226 respectively), are 0·514 and 0·517, in closer agreement with the remaining three values.

## Graphical Representation of Series Systems.

Since the wave numbers of the spectral lines always appear as differences of pairs of terms, the whole set of series and combinations may be very conveniently represented by plotting the "terms" which give rise to them. The various lines will then be represented by differences between the terms taken two by two. Such diagrams obviously have no necessary connection with any particular theory of spectra, but they are especially instructive when the terms are regarded as representing the stationary orbits of Bohr's theory.

Thus, for hydrogen, in place of drawing the orbits as in Fig. 9, it is convenient to plot the terms $N/m^2$ as in Fig. 11 ($m$ being an integer), and to regard them as representing small portions of the successive orbits, although they are not to the true scale of radii. Following a suggestion made by Birge,† the logarithms of the terms have been plotted, and not the terms themselves, as this has the advantage of

* Ann. d. Phys., **63**, 19 (1920).

† In a paper by Foote and Meggers, Phil. Mag., **40**, 80 (1920).

opening out the higher terms as compared with the lower. Regarding the lines as representing the non-radiating orbits, the nucleus is situated away to the right of the diagram, and the actual spectral lines correspond to the fall of electrons from orbits on the left to orbits on the right. By this method the three series of lines which would be required to represent the known spectrum of hydrogen are reduced to a single series of term values.

This simplification is of greater importance in connection with more complex spectra, as will appear from the examples given in Fig. 12. In all cases the terms plotted are those of the sharp, principal, diffuse and fundamental series, and these are distinguished by making the lines of different lengths. The two values for the terms of the principal series in doublets, or three terms in the case of triplets, are usually too close to be conveniently represented separately, and they have been indicated in the diagrams by breaking the corresponding lines into two or three equal portions, as the case may be. Similarly, the fact that there are sometimes two or three values of the diffuse series terms, arising from the presence of satellites, has been indicated by appropriate breaks in the upper portions of the lines.

The first diagram represents the orbit terms for the doublet system of sodium. The falls from the $\pi$ orbits to the innermost orbit, $1\sigma$, give the principal series, consisting of pairs with diminishing separation. The falls from the $\sigma$ and $\delta$ orbits to

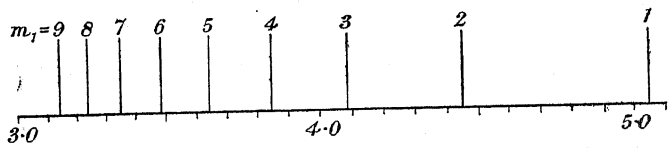


FIG. 11.—TERMS OF THE HYDROGEN SPECTRUM (log $N/m^2$).

the two adjacent orbits represented by $1\pi_1$ and $1\pi_2$, yield the constant separation pairs of the sharp and diffuse series respectively; falls from the $\varphi$ orbits to the orbit $2\delta$ give the fundamental series consisting of single lines. It will be seen that the various combinations can be considered in the same way. The orbits shown in the sodium diagram are 51 in number, and the lines which are actually represented in the tables by the various combinations of these terms are 98.

The second diagram represents in a similar manner the triplet system of magnesium. Here there are two sets of orbits, one corresponding to the triplets and the other to the singlets. There are no satellites. In the triplet system, the $1p$ orbits lie inside the 1s orbit; but the innermost orbit is that represented by $1S$. Inter-combinations between the two sets of orbits have been found to exist, as will appear from the tables.

The third diagram represents the doublet system of ionised magnesium, closely resembling the system of sodium. The term $1\delta$ is not certain, but analogy with calcium, strontium and barium suggests that it may exist. Also, according to Fowler's analysis, the observed series of fundamental type (which includes $\lambda$4481) has its limit at $2\delta$, and the separations of its constituent lines are out of step with the fundamental series of the other alkaline earth elements. The real fundamental series possibly has $1\delta$ for limit, and its lines in the extreme ultra-violet; but the absence of the lines $1\delta - 1\pi_{1,2}$ which appear in the other elements of the group, throws doubt on this interpretation. This diagram is of special interest in connection with the fact that while some of the enhanced lines of magnesium occur quite strongly

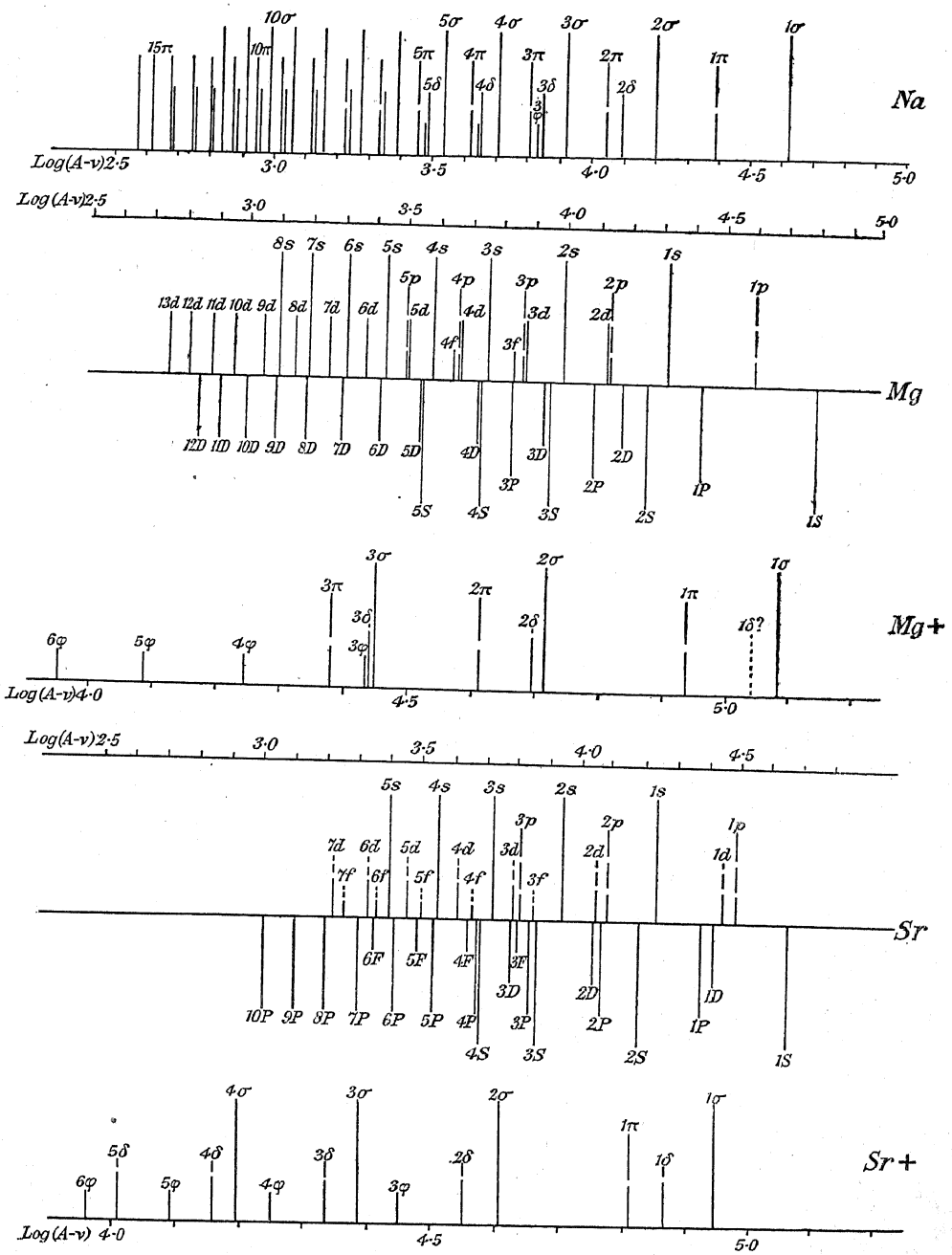


FIG. 12.—TERMS OF THE SPECTRA OF Na, Mg, Mg+, Sr, Sr+.

in the arc in air (*see* introduction to tables of magnesium series), there are others, belonging to the same series system, which only occur under spark conditions, or their equivalent in the arc *in vacuo*.* It was previously somewhat difficult to understand why the line 4481 ($2\delta$-$3\varphi$) did not appear simultaneously with lines like $\lambda$ 2795, 2802 ($1\sigma$—$1\pi_{1,2}$) in the arc in air, since all the lines belong to series with $4N$ for constant. In the light of Bohr's theory, as illustrated by the diagram, it would appear that in the arc in air the second electron is not removed to an indefinitely great distance from the nucleus, but only to a distance which is something less than the radius of the orbit corresponding to the term $3\varphi$. Under these conditions, there could be no combinations involving $3\varphi$ or any of the terms to the left of $3\varphi$ in the diagram. Under spark conditions, however, the stimulus is sufficient to remove two electrons to "infinity," so that the entire system of enhanced lines will be produced when one of the electrons returns. The return of the second electron would, of course, render the atom neutral, and the arc series would be developed.

The fourth diagram represents the triplet system of strontium, which is similar to that of magnesium, except that satellites are present in both the diffuse and fundamental series.

The last of the diagrams, for ionised strontium, is similar to the corresponding diagram for magnesium, except that satellites occur in the diffuse terms, and that the term $1\delta$ is certainly indicated by the observations. Since there are two values for $1\delta$, falls from the $\varphi$ orbits to $1\delta$ will yield doublets in the fundamental series.

In each case, of course, there may be other combinations of terms, or orbits, besides those which give rise to the four main series. Some of the combinations, however, are more probable than others, and these probabilities have been embodied by Bohr† in the so-called "selection principle."

## Ionisation Potentials and Spectral Series.

Experiments on the ionisation potentials of gases and vapours have an important bearing on Bohr's theory and upon the interpretation of some of the changes of spectra under different experimental conditions. In such experiments, the gas or vapour is bombarded by electrons from a glowing filament, and the electrons are accelerated by an adjustable electric field. The energy of the bombarding electrons is known from the potential difference through which they fall. Thus, if the potential difference is indicated by $V$ and the velocity of the electron by $v$,‡ we have

$$eV = \tfrac{1}{2}mv^2$$

In the case of hydrogen, Bohr's theory gives the negative energy corresponding to the different stationary orbits as

$$W_\tau = \frac{2\pi^2 me^4}{\tau^2 h^2}$$

where $\tau$ is the integer defining the orbit. This is equal to the energy required to remove the electron to an infinite distance from the nucleus.

* As a simple working hypothesis, it may be supposed that in air a large amount of energy is required to separate two electrons from the nucleus, while in the arc in vacuo a smaller amount of energy suffices on account of the greater freedom of movement of the electrons.

† Zeit. f. Phys., **2**, 423 (1920). *See* also Sommerfeld's book, p. 387.

‡ Since 1 volt $=10^8$ e.m.u.$=1/300$ e.s.u., and $e/m=1{\cdot}767\times10^7$ e.m.u.$=5{\cdot}301\times10^{17}$ e.s.u., the velocity corresponding to 1 volt will be about $5{\cdot}9\times10^7$ cm./sec.

When the electron passes from one orbit to a smaller one, it is assumed that the difference of energies is radiated as a quantum, $hn$, of frequency $n$; thus

$$W_{\tau_1}-W_{\tau_2}=\frac{2\pi^2me^4}{h^2}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=hn$$

so that

$$n=\frac{2\pi^2me^4}{h^3}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

or, if $\nu$ be the corresponding wave-number, and $c$ the velocity of light,

$$\nu=\frac{2\pi^2me^4}{ch^3}\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)=N\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

which is the formula already quoted for hydrogen.

We thus have

$$W_\tau=chN\,.\,\frac{1}{\tau^2}$$

and

$$W_{\tau_1}-W_{\tau_2}=chN\,.\left(\frac{1}{\tau_1^2}-\frac{1}{\tau_2^2}\right)$$

where $N$ is the Rydberg constant (in wave-number).

For series spectra in general, using the Rydberg formula for simplicity, we shall have

$$W_{\tau_1}-W_{\tau_2}=chN\left[\frac{1}{(\tau_1+\mu_1)^2}-\frac{1}{(\tau_2+\mu_2)^2}\right]$$

For comparison with the results of ionisation experiments, the work necessary to remove the electron from one orbit to another is most conveniently expressed in terms of equivalent volts, by putting $W_{\tau_1}-W_{\tau_2}=eV$, where $V$ is the potential difference through which the bombarding electron must fall to acquire the corresponding amount of energy. We thus get the general expression

$$V=\frac{chN}{e}\left[\frac{1}{(\tau_1+\mu_1)^2}-\frac{1}{(\tau_2+\mu_2)^2}\right]$$

or (in volts)*

$$V=\frac{N}{8102}\left[\frac{1}{(\tau_1+\mu_1)^2}-\frac{1}{(\tau_2+\mu_2)^2}\right]$$

If $\nu$ be the wave-number of the spectral line which is produced by the return of the electron from orbit $\tau_2$ to $\tau_1$, we have finally

$$V=\frac{\nu}{8102}$$

Since the ionisation potential corresponds to the removal of an electron from the innermost orbit to infinity, $\tau_2$ in this case $=\infty$, and the ionisation potential will be given by substituting for $\nu$ the limit of the series which extends furthest into the ultra-violet.

In the case of hydrogen, the innermost orbit is given by $\tau_1=1$, and $\nu=N/1^2=109678{\cdot}3$. Hence, the theoretical value of the ionisation potential of hydrogen

$$\frac{h}{e}=\frac{3\times10^{10}\times6{\cdot}545\times10^{-27}}{4{\cdot}774\times10^{-10}}\times300=\frac{1}{8102}$$

atoms is 13·5 volts. The experimental determinations are of this order, but are complicated by the fact that energy is required to dissociate the molecules before the atoms can be ionised.

The potential difference corresponding to the removal of an electron from the innermost orbit to the next one has been called the "resonance potential" or "radiation potential." The return of the electron to its normal position would then be followed by the emission of a single line, as observed by McLennan* and others in some elements. In hydrogen the wave-number of the resonance line would be $N\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=82{,}258$, and the resonance potential $82{,}258/8102=10{\cdot}1$ volts.

In the elements of Group I. the innermost orbit is that represented by the limit of the principal series; that is, by the term $1\sigma$ ($=1{\cdot}5$ $s$ of Ritz and Paschen). The second orbit is represented by the term $1\pi_1$ ($2p$ of Ritz and Paschen), and the frequency of the resonance line is that of the first principal line, $1\sigma-1\pi_1$ (*see* Na, Fig. 12). Hence, in Group I.,

$$I.P.=\frac{1\sigma}{8102}\text{ volts}$$

$$R.P.=\frac{1\sigma-1\pi_1}{8102}\text{ volts}$$

Caesium, as observed by Foote and Meggers,† furnishes an interesting example. Here we find $1\sigma=31{,}405$, and $1\sigma-1\pi_1=11{,}732$. The theoretical ionisation potential of caesium is therefore 3·876 volts, in remarkable accordance with the experimental value 3·9 volts. Similarly, the calculated resonance potential is 1·448 volts, in close accordance with the observed 1·5 volts. Similar results have also been obtained for sodium, potassium, zinc and cadmium.‡

In the triplet systems of Group II., which also include a singlet system (*see* Mg and Sr, Fig. 12), the innermost orbit connected with the arc spectra is indicated by the limit $1S$ of the principal series of singlets, and we accordingly have

$$I.P.=\frac{1S}{8102}$$

The second orbit is represented by the term $1p_1$ of the triplet system, but the resonance line actually observed is the combination $1S-1p_2$($=1{\cdot}5S-2p_2$ of Paschen). Thus, in this group

$$R.P.=\frac{1S-1p_2}{8102}$$

In mercury the resonance line $1S-1p_2$ is the well-known line in the ultra-violet $\lambda 2{,}536$, or $\nu 39{,}410$. The resonance potential of mercury is consequently $39{,}410/8102=4{\cdot}9$ volts. A second resonance potential corresponds with the line $1S-1P$, $=\lambda 1{,}849=\nu 54{,}066$, its magnitude being 6·7 volts. The term $1S$, $=84{,}177$, is the highest in the system of arc series, and the ionisation potential of mercury is accor-

* Proc. Roy. Soc., **A. 92**, 305 (1916).
† Phil. Mag., **40**, 80 (1920).
‡ Tate and Foote, Phil. Mag., **36**, 64 (1918).

dingly 10·4 volts. These values are in close accordance with experimental determinations.*

In calcium, two resonance potentials, and the ionisation potential, have been determined experimentally by Mohler, Foote and Stimson;† namely, 1·90, 2·85 and 6·01 volts. The corresponding theoretical values are

| | | |
|---|---|---|
| First resonance ... | ... $1S-1p_2=\lambda 6572{\cdot}78=\nu 15210{\cdot}3$ ; | $V=1{\cdot}887$ volts. |
| Second ,, ... | ... $1S-1P=\lambda 4226{\cdot}73=\nu 23652{\cdot}4$ ; | $V=2{\cdot}918$ volts. |
| Ionisation ... | ... $1S \quad =\lambda 2027{\cdot}56=\nu 49304{\cdot}8$ ; | $V=6{\cdot}081$ volts. |

The calcium series are similar to those of strontium illustrated in Fig. 12, and it will be observed that there is a preferential tendency for the electron to occupy orbits associated with principal series.

Helium is of considerable interest in this connection. Bohr's theory gives the total energy of the neutral helium atom as 6·13 times that of hydrogen,‡ so that the potential difference corresponding to the energy required to remove both electrons to infinity will be $6{\cdot}13\times 13{\cdot}5=82{\cdot}7$ volts. When the atom has already lost one electron, the energy necessary to remove the remaining electron is definitely given by the theory as four times that required for hydrogen, the equivalent in volts, therefore, being 54·0. This also follows from our formula, since the highest possible limit is $4N^1/1^2=438{,}892$, which, divided by 8,102, $=54{\cdot}2$ volts. For the first ionisation the theory accordingly gives the ionisation potential as $82{\cdot}7-54{\cdot}0=28{\cdot}7$ volts. It is not yet possible to predict the spectral lines of the neutral atom, but the theory thus points to $28{\cdot}7\times 8{,}102$, $=\nu 232{,}530$, $=\lambda 430$ as the highest limit in the helium spectrum.

Experiments appear to show that the first ionisation actually occurs at 25·5 volts, and the first radiation at about 20 volts.§ The innermost orbit would thus correspond to a series limit in the region of $25{\cdot}5\times 8{,}102=\nu 206{,}600$, $=\lambda 484A$, and a resonance line would be expected at about $20\times 8{,}102=\nu 162{,}040$, $=\lambda 605A$. Experimental evidence of the probable existence of such frequencies in the spectrum of helium is furnished by the work of Richardson and Bazzoni‖ on the high-frequency limits of the spectrum of this gas. The highest frequency thus determined was found to lie between $\lambda 470$ and $\lambda 420$, and probably nearer to the latter value, in general agreement with $\lambda 430$ for the limit of the series calculated from Bohr's theoretical value of the ionisation potential.

Indirect evidence of the existence of lines in the far ultra-violet is also afforded by the fact that none of the known lines of helium appear as absorption lines until the gas is submitted to an electric discharge. This is also the case with the Balmer series of hydrogen and suggests that the limit of the so-called principal series of helium does not represent the innermost, or normal, orbit. In the alkali metals, the lines of the principal series are readily reversed at low temperatures, and the innermost orbits are represented by the limits of these series.

* Franck and Hertz, Verh. d. D. Phys. Ges., **15**, 34 (1913). Davis and Goucher, Phys. Rev., **10**, 84 (1917).

† Phil. Mag., **40**, 73 (1920).

‡ Phil. Mag., **26**, 489 (1913).

§ Horton and Davies. Proc. Roy. Soc., A. **95**, 408 (1919); Phil. Mag., **39**, 592 (1920); Compton and Lilly, Astrophys. Jour., **52**, 1 (1920).

‖ Phil. Mag., **34**, 285 (1917).

The excitation of the enhanced lines of helium, corresponding to the second ionisation, has been found to require a potential difference of 80 volts, in good agreement with the theoretical value.*

It will be gathered that a very important field of research has been opened up by these investigations of the connection between spectral series and the resonance and ionisation potentials. They not only provide valuable tests of theories of the origin of spectra, but may help in the detection of series in spectra which have not yet been resolved. In a doublet system (compare caesium, p. 70) the limit of the principal series, and the first line, could be calculated with fair approximation from the observed values of the ionisation and radiation potentials, and thence all the lines of the series; from the principal series, the sharp series could also be calculated approximately from the Rydberg relations. Similarly, the principal series of singlets in a triplet system could be calculated from the ionisation potential and the second resonance potential, if it be established that the examples given above are typical.†

## Spectral Series and the Periodic Table.

The analysis of spectra into their component series is not yet sufficiently complete to permit a full discussion of the relation between the spectra and the positions of the elements in the periodic classification, but there are several points of interest in this connection.

In the first place, it is to be observed that all the elements of the same group give series of the same type, so far as they are known. Omitting the inert gases, and referring first to the "arc" spectra yielded by neutral atoms, the elements of Group I. present doublet systems, those of Group II. triplets, and those of Group III. doublets. The remaining groups have not yet been completely sorted out into series. In Group IV., probable series lines have only at present been identified in silicon, which gives triplets in the arc. In Group V. no series have yet been traced. Oxygen, sulphur, and selenium of Group VI., however, give triplets.

The interesting point is that doublets and triplets appear to alternate with each other through the first six groups. Since the number of the group is supposed to indicate the valency (and also the number of electrons in the outer ring), it would seem that elements of even valency yield triplets, while those of odd valency give rise to doublets. The only known exception is manganese, which gives triplets in the arc, whereas doublets would be expected according to the rule stated; the triplets, however, have not the same simplicity as those which occur in Group II., and there appears to be some doubt as to the number of electrons in the outer ring (Sommerfeld, p. 304).

The elements of Group II., which give triplets in the arc, give series of enhanced doublets in the spark. Those of Group III., so far as the series are known, give doublets in the arc, and evidence of the occurrence of triplets in the spark spectra of Al, Sc, Y, has been found by Popow. Elements of Group I., which give doublets in the arc, give spark spectra which have not been resolved into series, as in most of the inert gases.

Thus, so far as these observations permit deductions, the spark spectrum of

* Rau. Sitz. Ber. d. Phys. Med. Ges. zu. Würzburg (1914), p. 20; Compton and Lilly, loc. cit.

† Since the above was written, an important "Report on Photo-electricity, including Ionising and Radiating Potentials," by Prof. A. L. Hughes, has been issued by the National Research Council, Washington (Bulletin, No. 10, 1921).

*Periodic Classification of the Elements.*

| | 0. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
|---|---|---|---|---|---|---|---|---|---|
| 1. H 1·008 | | | | | | | | | |
| | 2. He 4·0 | 3. Li 7·0 | 4. Be 9·1 | 5. B 10·9 | 6. C 12·0 | 7. N 14·01 | 8. O 16·00 | 9. F 19·0 | |
| | 10. Ne 20·2 | 11. Na 23·00 | 12. Mg 24·32 | 13. Al 27·1 | 14. Si 28·3 | 15. P 31·0 | 16. S 32·07 | 17. Cl 35·46 | |
| | 18. A 39·9 | 19. K 39·10<br>29. Cu 63·56 | 20. Ca 40·1<br>30. Zn 65·38 | 21. Sc 44·1<br>31. Ga 69·9 | 22. Ti 48·1<br>32. Ge 72·5 | 23. V 51·2<br>33. As 74·96 | 24. Cr 52·0<br>34. Se 79·2 | 25. Mn 54·9<br>35. Br 79·9 | 26. Fe 55·8 27. Co 58·97 28. Ni 58·68 |
| | 36. Kr 82·9 | 37. Rb 85·45<br>47. Ag 107·88 | 38. Sr 87·63<br>48. Cd 112·4 | 39. Y 88·8<br>49. In 114·8 | 40. Zr 90·6<br>50. Sn 119·0 | 41. Nb 93·2<br>51. Sb 120·2 | 42. Mo 96·0<br>52. Te 127·5 | 43. ...<br>53. I 126·9 | 44. Ru 101·7 45. Rh 102·9 46. Pd 106·7 |
| | 54. Xe 130·2 | 55. Cs 132·8<br>79. Au 197·2 | 56. Ba 137·37<br>80. Hg 200·4 | 57–71 Rare Earths<br>81. Tl 204·0 | 72. ...<br>82. Pb 207·1 | 73. Ta 181·2<br>83. Bi 208·0 | 74. W 184·0<br>84. Po | 75. ...<br>85. ... | 76. Os 190·9 77. Ir 193·1 78. Pt 195·2 |
| | 86. Nt (Em) 222·4 | 87. ... | 88. Ra 226·4 | 89. Ac 226 | 90. Th 232·2 | 91. $Ux_2$ 234 | 92. U 238·2 | | |
| Neutral atoms ...R<br>Ionised atoms ...R+<br>Second ionisation R++<br>Third ionisation R+++ | | *d* *d* | *t* *t*<br>*d* *d* | *d*<br>*t* ? | *t*(Si)<br>*d*(C, Si)<br>*t*?(C, Si)<br>*d*?(C, Si) | *d*?(N) | *t*<br>*d*?(O) | *t*(Mn)<br>*t*?(F,Cl) | *d*=doublets<br>*t*=triplets |

an element has the same character as the arc spectrum of the element adjacent to it in the preceding group of the periodic table. This relation is explicable on the supposition that the loss of an electron from the outer ring reduces the valency of the element by 1 and so displaces it to the preceding group. Attention was first directed to this relation by Kossel and Sommerfeld,* who have called it the *displacement law*, from analogy with the displacement law in radio-activity.

Further evidence in support of this "law" is given by certain unpublished observations made by the author. In Group IV., definite series of enhanced doublets, with $4N$ for constant, have been identified in carbon and silicon. There is evidence also of a "second-step" ionisation in each of these elements ($C^{++}$ and $Si^{++}$) giving triplets and possibly representing a displacement of two places to the left in the table; and of a "third-step" ionisation ($C^{+++}$ and $Si^{+++}$) represented by a system of doublets and corresponding to a possible displacement of three places to the left. A final test of these suggestions requires the extension of the observations into the far ultra-violet so as to permit calculations of the series constants, which should be $9N$ and $16N$ respectively. In Group V. there are doublets among the spark lines of nitrogen which possibly represent the second-step ionisation, $N^{++}$. In Group VI. the second, or spark, spectrum of oxygen shows several doublets which perhaps represent $O^{+}$. In Group VII. fluorine and chlorine show triplets under spark conditions, which, however, have not yet been arranged in series.

These observations are summarised in the accompanying table of the elements, in which it is to be understood that *d* ? and *t* ? indicate that the evidence is not complete.

On theoretical grounds Kossel and Sommerfeld also suggested a possible numerical relation between the spark spectrum of an element and the arc spectrum of the element which precedes it in the periodic table. Since the doublet separation in the subordinate series is determined by the difference of limits $1\pi_1-1\pi_2$, the fact that the series constant for the ionised elements is four times that for neutral atoms suggested that the spark doublets of Group II., for example, would have approximately four times the separation of the doublets in the arc spectra of corresponding elements of Group I. They gave the following figures in support :—

| Spark series, $\Delta\nu$. | | Arc series, $\Delta\nu'$. | | Ratio, $\Delta\nu/\Delta\nu'$. |
|---|---|---|---|---|
| $Mg^{+}$ | 91·5 | Na | 17·21 | $Mg^{+}$ : Na=5·3 |
| $Ca^{+}$ | 223 | K | 57·90 | $Ca^{+}$ : K=3·9 |
| $Sr^{+}$ | 800 | Rb | 237·71 | $Sr^{+}$ : Rb=3·4 |
| $Ba^{+}$ | 1691 | Cs | 554·10 | $Ba^{+}$ : Cs=3·1 |
| $Zn^{+}$ | 872 | Cu | 248·1 | $Zn^{+}$ : Cu=3·5 |
| $Cd^{+}$ | 2484 | Ag | 920·6 | $Cd^{+}$ : Ag=2·7 |

The ratios show a systematic decrease with increase of atomic weight, but the question will doubtless be further investigated. Similar data were also given comparing the imperfectly known spark triplets of Group III. with the arc triplets of Group II., showing ratios ranging from 2·2 to 5·0.

An attempt to trace further numerical relations between the series of the ionised elements of Group II. and the neutral elements of Group I. has been made by Fues,† on the ground of Sommerfeld's theoretical deductions ("Atombau," pp. 295, 511). In the extended Ritz formula, where the denominator is $[m+a+\alpha(m, a)+\alpha'(m, a)^2+\ldots]^2$:

* Verh. d. D. Phys. Ges., **21**, 240 (1919).
† Ann. d. Phys., **63**, 1 (1920).

for arc spectra, and $[m+a^*+\alpha^*(m, a^*)+\ldots]^2$ for enhanced series, it is considered that in a first approximation $a^*$ for a singly-ionised atom of atomic number Z should have twice the value of $a$ for the neutral atom of atomic number Z−1. In the sharp series $a=\sigma$, and in the principal series $a=\pi$, and with the Ritz numeration, having $m=1{\cdot}5,\ldots$ in the sharp series, and $m=2, 3, \ldots$ in the principal series, the constants for some of the spectra are as follows :—

| | $\sigma, \sigma^*$ | $\pi_1, \pi_1^*$ |
|---|---|---|
| Na | +0·15 | +0·15 |
| $Mg^+$ | +0·43 | +0·305 |
| K | +0·325 | +0·29 |
| $Ca^+$ | +0·70 | +0·5±0·15 |
| Rb | +0·31 | +0·36 |
| $Sr^+$ | −0·815 | +0·61±0·15 |
| Cs | +0·45 | +0·45 |
| $Ba^+$ | +0·93 | +0·75 |

It will be seen that the relation is in some cases approximately fulfilled, but would not hold for the sharp series if integral values were assigned to $m$. Investigations of this nature are evidently of importance in connection with theories of spectra, and may perhaps give indications as to the best type of series formula.

The question of the relation of the spectral series to the grouping of the elements in the periodic table calls for much further investigation of the spectra which have not yet been resolved into series. So far as the inquiry has gone, however, the results are very suggestive as to the kind of series to be expected in the spectrum of an element, and may be of considerable assistance in guiding further research.

# APPENDIX I.

*Calculation of Formula Constants.*

Probably the most generally useful formulæ are those of Ritz and Hicks, and it will suffice to indicate the methods of determining the constants in the case of the latter, namely

$$\nu = A - \frac{N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}$$

From the observational data it will be advisable, as a rule, to choose the wave-numbers of the two least refrangible lines, and one of the most refrangible, since the former have most effect on the second term and the latter have the greatest influence on the limit. In all cases an approximate value of the limit should first be obtained by reference to Rydberg's interpolation table, as explained on p. 28. When an approximate value of $\mu$ is also required, it may be obtained from the same source.

*Successive Approximation.*

Let $\nu_1$, $\nu_2$, $\nu_3$ be the wave-numbers of three lines selected for the determination of constants, and let $m$, $m+p$, $m+q$ be the corresponding order-numbers. Further, let

$$m\sqrt{\frac{N}{A-\nu_1}}=a\ ;\ (m+p)\sqrt{\frac{N}{A-\nu_2}}=b\ ;\ \text{and}\ (m+q)\sqrt{\frac{N}{A-\nu_3}}=c$$

Then a value of $A$ has to be found which satisfies the relation

$$p(c-b)-(q-p)(b-a)=pq(q-p)$$

Beginning with the approximate value of $A$ determined from Rydberg's table, a few trials will lead to the true value. We then have

$$\mu=\frac{b-a}{p}-(2m+p)=\frac{c-b}{q-p}-(2m+p+q)$$

and

$$\alpha=a-m(m+\mu)=b-(m+p)(m+p+\mu)=c-(m+q)(m+q+\mu).$$

When three consecutive lines are selected, $p=1$ and $q=2$, and the relation to be satisfied by trials of $A$ becomes

$$(c-b)-(b-a)=2$$

*Hicks's Method.*

A more direct solution has been given by Hicks.* An approximate value of $A$ having been determined as before, the series is supposed given by

$$\nu = A + x - \frac{N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}$$

* Phil. Mag., **30**, 734 (1915).

where $x$ is the correction to the limit, and $x$, $\mu$, $\alpha$ are to be determined from three successive wave-numbers $\nu$. Binomial expansion gives

$$m+\mu+\frac{\alpha}{m}=\frac{\sqrt{N}}{(A-\nu+x)^{\frac{1}{2}}}=\frac{\sqrt{N}}{(A-\nu)^{\frac{1}{2}}}-\frac{\sqrt{N}}{2(A-\nu)^{\frac{3}{2}}}\,x=(m+d_m)-\gamma_m x \text{ (say)}$$

$$\therefore\ m\mu+\alpha=md_m-m\gamma_m x$$

Differencing,

$$\mu=\Delta(md_m)-x\Delta(m\gamma_m)$$
$$o=\Delta^2(md_m)-x\Delta^2(m\gamma_m),$$

whence

$$x=\frac{\Delta^2(md_m)}{\Delta^2(m\gamma_m)},$$

and $\mu$ and $\alpha$ are then easily calculated. Hicks gives the following example from a series of oxygen lines in which the three consecutive wave-numbers are 10791·32, 16233·52, and 18753·65. The limit is 23,194$+x$.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | (1) | 10791·32 | | 16233·52 | | 18753·65 | |
| $A-\nu$ | (2) | 12402·68 | (3)−(1) | 6960·48 | | 4440·35 | |
| log $A-\nu$ | (3) | 4·0935156 | $\bar{4}$·37978 | 3·8426392 | $\bar{4}$·75610 | 3·6474172 | $\bar{3}$·04893 |
| log $N/A-\nu$ | (4) | 0·9465921 | 0·0002397 | 1·1974685 | 0·0005703 | 1·3926907 | 0·0011196 |
| ½ log $N/A-\nu$ | (5) | 0·4732960 | 0·0001198 | 0·5987342 | 0·0002851 | 0·6963453 | 0·0005592 |
| $\sqrt{\frac{N}{A-\nu}}$ | | 2·973693 | | 3·969484 | | 4·969873 | |

| | | | | | |
|---|---|---|---|---|---|
| 1·947386 | | | 0·0002396 | | |
| | 0·961066 | | | 0·0006157 | |
| 2·908452 | | 0·009974 | 0·0008553 | | 0·0007674 |
| | 0·971040 | | | 0·0013831 | |
| 3·879492 | | | 0·0022384 | | |

$$x=\frac{0\cdot009974}{0\cdot0007674}=13\cdot00 \qquad A=23194\cdot00+13\cdot00=23207\cdot00$$

$$\mu=0\cdot961066-(13\times0\cdot0006157)$$
$$\begin{array}{r}0\cdot008004\\ \hline 0\cdot953062\end{array}$$

$$\alpha=1\cdot947386-13\times0\cdot0002396-2\mu \qquad \begin{array}{r}0\cdot003114\\ 1\cdot906124\\ \hline 1\cdot909238\end{array}$$
$$\begin{array}{r}1\cdot909238\\ \hline 0\cdot038148\end{array}$$

$$\nu=23207\cdot00-N/\left[m+0\cdot953062+\frac{0\cdot038148}{m}\right]^2$$

In each of the above main columns the first number is $\nu$, the second $(A-\nu)$, the third log. $(A-\nu)$, the fourth log. $N/(A-\nu)$ obtained by subtracting the third from log. $N$ (taken as 5·0401077 in the above example), the fifth is half the fourth, and the sixth is $\sqrt{N}/\sqrt{A-\nu}$, or $(m+d_m)$. The third is then subtracted from the

fifth and written down on the right, being the log. of $N^{\frac{1}{2}}/(A-\nu)^{\frac{3}{2}}$; below this is the antilog., which, divided by two, gives $\gamma_m$.

The decimal parts of $\sqrt{N}/\sqrt{(A-\nu)}$ at the bottom of the main columns are next multiplied by the respective integers $m$ (in this case 2, 3, 4) and differenced twice. Similarly with the $\gamma$ terms, the work being on the right. The constants are then readily determined.

A valuable feature of this method is that if the limits of error of the observations be known, their effects on the values of the constants can readily be found by calculating $\partial x$, $\partial \mu$, $\partial \alpha$.

When the term $\beta/m^2$ is introduced into the original formula, four lines are necessarily to be used; the $d_m$, $\gamma_m$ are then to be multiplied by $m^2$, and differenced three times. Then

$$x=\frac{\Delta^3(m^2d_m)}{\Delta^3(m^2\gamma_m)}\,;\quad 2\mu=\Delta^2(m^2d_m)-x\Delta^2(m^2\gamma_m)$$

$$\alpha=\Delta(m^2d_m)-x\Delta(m^2\gamma_m)-(2m+1)\mu$$

$$\beta=m^2d_m-m^2\gamma_m x-m\alpha-m^2\mu$$

When wave-numbers are derived from data on the international scale the value of $N$ should be taken as 109678·3, or log. $N$=5·0401278.

### *The Differential Method.*

The differential method is generally applicable to series formulæ. In the case of the Hicks formula we have

$$\Delta\nu=\Delta A+\frac{2N}{\left(m+\mu+\frac{\alpha}{m}\right)^3}\left(\Delta\mu+\frac{\Delta\alpha}{m}\right)$$

Approximate values of $A$ and $\mu$ being determined from Rydberg's table, and $\alpha$ being supposed zero, the values of $\Delta\nu$, being the differences between the observed and calculated wave-numbers, are obtained for the three lines selected for the determination of constants. The values of $\Delta A$, $\Delta\mu$, and $\Delta\alpha$ ($=\alpha$ in this case) can then be determined from the three resulting linear equations. If $\alpha$ be large, it will be necessary to recalculate the constants, including an approximate value of $\alpha$ in the first equations when the $\Delta\nu$ are calculated.

When it is desired to investigate the value of $N$, four lines must be used, and a similar procedure adopted, with four equations of the form

$$\Delta\nu=\Delta A-\frac{\Delta N}{\left(m+\mu+\frac{\alpha}{m}\right)^2}+\frac{2N}{\left(m+\mu+\frac{\alpha}{m}\right)^3}\left(\Delta\mu+\frac{\Delta\alpha}{m}\right)$$

If a term $\beta/m^2$ be introduced into the original formula, the procedure is similar but rather more complex.

The differential method is obviously adapted for a least square solution, in which all the observed lines may be utilised in the calculation of constants. The numerical work involved, however, is rather laborious, and there is not much point in forcing a series of observations into an imperfect formula.

*Determination of Limits in Special Cases.*

In the case of series which do not closely follow the formulae of Ritz or Hicks, other methods of determining the limits have to be adopted. In a communication to the author, Prof. Saunders has explained that his procedure is first to make some reasonable assumption as to the limit (say, from a graphical construction), and then to calculate the values of $[m+\mu+f(m)]$ from the corresponding terms $(A-\nu)$ for the later lines. The values of $[\mu+f(m)]$ are then plotted against $m$, and if the curve shows an inflexion another limit is tried. By successive trials the limit is thus obtained within a few units if several members of the series have been observed. The result can often be checked by other series relationships, as, for instance, that the sharp and diffuse series must have the same limit, or that the first term of the principal series must correspond with the limit of the sharp series. Combination of terms from different systems also gives an important check, as in the case of $1S-1p_2$. Saunders's plan is to adjust the limits so as to satisfy as many as possible of these conditions.

The method adopted by Nicholson in the case of helium (*see* p. 34) would probably also be useful in this connection, since it is possible to use all the lines of a series in calculating the limits.

# APPENDIX II.

## TABLES FOR COMPUTATIONS.

TABLE I.—*Corrections to reduce Wave-lengths from Rowland's scale to the international scale.*

| Region. | Subtract. | Region. | Subtract. | Region. | Subtract. |
|---|---|---|---|---|---|
| λ 8800–8300 | 0·35 | λ 6500–6050 | 0·21 | λ 3450–3250 | 0·14 |
| 8300–8200 | 0·31 | 6050–5500 | 0·22 | 3250–3125 | 0·13 |
| 8200–8000 | 0·30 | 5500–5400 | 0·21 | 3125–2950 | 0·12 |
| 8000–7700 | 0·29 | 5400–5375 | 0·20 | 2950–2800 | 0·11 |
| 7700–7400 | 0·28 | 5375–5325 | 0·19 | 2800–2625 | 0·10 |
| 7400–7200 | 0·27 | 5325–5300 | 0·18 | 2625–2475 | 0·09 |
| 7200–7000 | 0·26 | 5300–5125 | 0·17 | 2475–2300 | 0·08 |
| 7000–6850 | 0·25 | 5125–4550 | 0·18 | 2300–2150 | 0·07 |
| 6850–6750 | 0·24 | 4550–4350 | 0·17 | 2150–1950 | 0·06 |
| 6750–6570 | 0·23 | 4350–4150 | 0·16 | | |
| 6570–6500 | 0·22 | 4150–3450 | 0·15 | | |

The corrections from 8800 to 7000 are as given by Meggers; the remainder are as given by Kayser. At 10,000A the correction will be about 0·43A.

TABLE IIA.—*Correction to Vacuum of Wave-lengths in Infra-Red.*

The following corrections have been calculated from the Washington formula for 15° C. and 760 mm. It is not certain that the formula is accurately applicable to this region.

| λ in air. | Add λ (μ—1) | Diff. | λ in air. | Add λ (μ—1) | Diff. |
|---|---|---|---|---|---|
| 10,000 | 2·74 | | 15,000 | 4·10 | |
| | | 0·27 | | | 1·35 |
| 11,000 | 3·01 | | 20,000 | 5·45 | |
| | | 0·27 | | | 2·73 |
| 12,000 | 3·28 | | 30,000 | 8·18 | |
| | | 0·27 | | | 2·73 |
| 13,000 | 3·55 | | 40,000 | 10·91 | |
| | | 0·28 | | | 2·72 |
| 14,000 | 3·83 | | 50,000 | 13·63 | |
| | | 0·27 | | | 2·73 |
| 15,000 | 4·10 | | 60,000 | 16·36 | |

TABLE II.—*Correction to Vacuum of Wave-lengths in Air at* 15° *C. and* 760 *mm.*

| λ in air. | Add λ (μ—1) | Diff. | λ in air. | Add λ (μ—1) | Diff. | λ in air. | Add λ (μ—1) | Diff. |
|---|---|---|---|---|---|---|---|---|
| 2000 | 0·6512 | | 4500 | 1·2581 | | 7400 | 2·0350 | |
| | | 89 | | | 264 | | | 270 |
| 50 | 0·6601 | | 4600 | 1·2845 | | 7500 | 2·0620 | |
| | | 94 | | | 265 | | | 271 |
| 2100 | 0·6695 | | 4700 | 1·3110 | | 7600 | 2·0891 | |
| | | 96 | | | 265 | | | 270 |
| 50 | 0·6791 | | 4800 | 1·3375 | | 7700 | 2·1161 | |
| | | 100 | | | 265 | | | 270 |
| 2200 | 0·6891 | | 4900 | 1·3640 | | 7800 | 2·1431 | |
| | | 102 | | | 266 | | | 271 |
| 50 | 0·6993 | | 5000 | 1·3906 | | 7900 | 2·1702 | |
| | | 104 | | | 267 | | | 270 |
| 2300 | 0·7097 | | 5100 | 1·4173 | | 8000 | 2·1972 | |
| | | 107 | | | 266 | | | 271 |
| 50 | 0·7204 | | 5200 | 1·4439 | | 8100 | 2·2243 | |
| | | 109 | | | 267 | | | 270 |
| 2400 | 0·7313 | | 5300 | 1·4706 | | 8200 | 2·2513 | |
| | | 222 | | | 267 | | | 271 |
| 2500 | 0·7535 | | 5400 | 1·4973 | | 8300 | 2·2784 | |
| | | 229 | | | 267 | | | 270 |
| 2600 | 0·7764 | | 5500 | 1·5240 | | 8400 | 2·3054 | |
| | | 233 | | | 268 | | | 271 |
| 2700 | 0·7997 | | 5600 | 1·5508 | | 8500 | 2·3325 | |
| | | 238 | | | 267 | | | 271 |
| 2800 | 0·8235 | | 5700 | 1·5775 | | 8600 | 2·3596 | |
| | | 241 | | | 268 | | | 271 |
| 2900 | 0·8476 | | 5800 | 1·6043 | | 8700 | 2·3867 | |
| | | 245 | | | 268 | | | 270 |
| 3000 | 0·8721 | | 5900 | 1·6311 | | 8800 | 2·4137 | |
| | | 247 | | | 269 | | | 271 |
| 3100 | 0·8968 | | 6000 | 1·6580 | | 8900 | 2·4408 | |
| | | 249 | | | 268 | | | 271 |
| 3200 | 0·9217 | | 6100 | 1·6848 | | 9000 | 2·4679 | |
| | | 252 | | | 269 | | | 271 |
| 3300 | 0·9469 | | 6200 | 1·7117 | | 9100 | 2·4950 | |
| | | 253 | | | 269 | | | 271 |
| 3400 | 0·9722 | | 6300 | 1·7386 | | 9200 | 2·5221 | |
| | | 255 | | | 269 | | | 271 |
| 3500 | 0·9977 | | 6400 | 1·7655 | | 9300 | 2·5492 | |
| | | 256 | | | 269 | | | 271 |
| 3600 | 1·0233 | | 6500 | 1·7924 | | 9400 | 2·5763 | |
| | | 257 | | | 269 | | | 272 |
| 3700 | 1·0490 | | 6600 | 1·8193 | | 9500 | 2·6035 | |
| | | 259 | | | 269 | | | 271 |
| 3800 | 1·0749 | | 6700 | 1·8462 | | 9600 | 2·6306 | |
| | | 259 | | | 270 | | | 271 |
| 3900 | 1·1008 | | 6800 | 1·8732 | | 9700 | 2·6577 | |
| | | 260 | | | 269 | | | 271 |
| 4000 | 1·1268 | | 6900 | 1·9001 | | 9800 | 2·6848 | |
| | | 262 | | | 270 | | | 271 |
| 4100 | 1·1530 | | 7000 | 1·9271 | | 9900 | 2·7119 | |
| | | 262 | | | 270 | | | 272 |
| 4200 | 1·1792 | | 7100 | 1·9541 | | 10000 | 2·7391 | |
| | | 262 | | | 270 | | | |
| 4300 | 1·2054 | | 7200 | 1·9811 | | | | |
| | | 263 | | | 269 | | | |
| 4400 | 1·2317 | | 7300 | 2·0080 | | | | |
| | | 264 | | | | | | |

$\lambda_{vac.} = \mu\lambda_{air}$. $\Delta\lambda = \lambda_{vac.} - \lambda_{air} = \lambda_{air}\ (\mu - 1)$.

TABLE III.—*Rydberg's Interpolation Table (revised).*

Values of the Function $109678{\cdot}3/(m+\mu)^2$.

| $\mu$ | 1 | $\Delta\nu$ | 2 | $\Delta\nu$ | 3 | $\Delta\nu$ | 4 | $\Delta\nu$ | 5 | $\Delta\nu$ | 6 | $\Delta\nu$ | 7 | $\Delta\nu$ | 8 | $\Delta\nu$ | 9 | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·00 | 109678 | *82258* | 27420 | *15233* | 12187 | *5332* | 6855 | *2468* | 4387 | *1340* | 3047 | *809* | 2238 | *524* | 1714 | *360* | 1354 | 0·00 |
| 0·01 | 107517 | *80370* | 27147 | *15041* | 12106 | *5285* | 6821 | *2451* | 4370 | *1333* | 3037 | *805* | 2232 | *523* | 1709 | *358* | 1351 | 0·01 |
| 0·02 | 105419 | *78540* | 26879 | *14853* | 12026 | *5239* | 6787 | *2435* | 4352 | *1326* | 3026 | *801* | 2225 | *520* | 1705 | *357* | 1348 | 0·02 |
| 0·03 | 103382 | *76767* | 26615 | *14669* | 11946 | *5193* | 6753 | *2418* | 4335 | *1319* | 3016 | *797* | 2219 | *518* | 1701 | *356* | 1345 | 0·03 |
| 0·04 | 101404 | *75049* | 26355 | *14487* | 11868 | *5148* | 6720 | *2402* | 4318 | *1312* | 3006 | *793* | 2213 | *516* | 1697 | *355* | 1342 | 0·04 |
| 0·05 | 99481 | *73383* | 26098 | *14308* | 11790 | *5103* | 6687 | *2386* | 4301 | *1304* | 2997 | *790* | 2207 | *514* | 1693 | *354* | 1339 | 0·05 |
| 0·06 | 97613 | *71767* | 25846 | *14133* | 11713 | *5059* | 6654 | *2370* | 4284 | *1297* | 2987 | *787* | 2200 | *512* | 1688 | *352* | 1336 | 0·06 |
| 0·07 | 95797 | *70200* | 25597 | *13960* | 11637 | *5016* | 6621 | *2354* | 4267 | *1290* | 2977 | *783* | 2194 | *510* | 1684 | *351* | 1333 | 0·07 |
| 0·08 | 94031 | *68680* | 25351 | *13789* | 11562 | *4973* | 6589 | *2339* | 4250 | *1283* | 2967 | *779* | 2188 | *508* | 1680 | *350* | 1330 | 0·08 |
| 0·09 | 92314 | *67205* | 25109 | *13622* | 11487 | *4930* | 6557 | *2324* | 4233 | *1276* | 2957 | *775* | 2182 | *506* | 1676 | *349* | 1327 | 0·09 |
| 0·10 | 90643 | *65773* | 24870 | *13457* | 11413 | *4888* | 6525 | *2308* | 4217 | *1269* | 2948 | *772* | 2176 | *504* | 1672 | *347* | 1325 | 0·10 |
| 0·11 | 89017 | *64382* | 24635 | *13296* | 11339 | *4847* | 6492 | *2292* | 4200 | *1262* | 2938 | *768* | 2170 | *502* | 1668 | *346* | 1322 | 0·11 |
| 0·12 | 87435 | *63032* | 24403 | *13136* | 11267 | *4806* | 6461 | *2277* | 4184 | *1256* | 2928 | *765* | 2163 | *500* | 1663 | *344* | 1319 | 0·12 |
| 0·13 | 85894 | *61719* | 24175 | *12980* | 11195 | *4765* | 6430 | *2262* | 4168 | *1249* | 2919 | *762* | 2157 | *498* | 1659 | *343* | 1316 | 0·13 |
| 0·14 | 84394 | *60445* | 23949 | *12825* | 11124 | *4725* | 6399 | *2248* | 4151 | *1242* | 2909 | *758* | 2151 | *496* | 1655 | *342* | 1313 | 0·14 |
| 0·15 | 82933 | *59206* | 23727 | *12674* | 11053 | *4685* | 6368 | *2233* | 4135 | *1235* | 2900 | *755* | 2145 | *494* | 1651 | *341* | 1310 | 0·15 |
| 0·16 | 81509 | *58001* | 23508 | *12524* | 10984 | *4646* | 6338 | *2219* | 4119 | *1228* | 2891 | *752* | 2139 | *492* | 1647 | *340* | 1307 | 0·16 |
| 0·17 | 80122 | *56830* | 23292 | *12377* | 10915 | *4608* | 6307 | *2204* | 4103 | *1222* | 2881 | *748* | 2133 | *490* | 1643 | *339* | 1304 | 0·17 |
| 0·18 | 78769 | *55691* | 23078 | *12232* | 10846 | *4569* | 6277 | *2189* | 4088 | *1216* | 2872 | *744* | 2128 | *489* | 1639 | *337* | 1302 | 0·18 |
| 0·19 | 77451 | *54583* | 22868 | *12090* | 10778 | *4531* | 6247 | *2175* | 4072 | *1209* | 2863 | *741* | 2122 | *487* | 1635 | *336* | 1299 | 0·19 |
| 0·20 | 76166 | *53505* | 22661 | *11950* | 10711 | *4494* | 6217 | *2161* | 4056 | *1203* | 2853 | *737* | 2116 | *485* | 1631 | *335* | 1296 | 0·20 |
| 0·21 | 74912 | *52456* | 22456 | *11812* | 10644 | *4456* | 6188 | *2147* | 4041 | *1197* | 2844 | *734* | 2110 | *483* | 1627 | *334* | 1293 | 0·21 |
| 0·22 | 73689 | *51435* | 22254 | *11676* | 10578 | *4419* | 6159 | *2134* | 4025 | *1190* | 2835 | *731* | 2104 | *481* | 1623 | *333* | 1290 | 0·22 |
| 0·23 | 72495 | *50440* | 22055 | *11542* | 10513 | *4383* | 6130 | *2120* | 4010 | *1184* | 2826 | *728* | 2098 | *479* | 1619 | *332* | 1287 | 0·23 |
| 0·24 | 71331 | *49472* | 21859 | *11411* | 10448 | *4347* | 6101 | *2107* | 3994 | *1177* | 2817 | *725* | 2092 | *477* | 1615 | *331* | 1284 | 0·24 |
| 0·25 | 70194 | *48529* | 21665 | *11281* | 10384 | *4312* | 6072 | *2093* | 3979 | *1171* | 2808 | *721* | 2087 | *475* | 1612 | *330* | 1282 | 0·25 |
| 0·26 | 69084 | *47611* | 21473 | *11153* | 10320 | *4276* | 6044 | *2080* | 3964 | *1165* | 2799 | *718* | 2081 | *473* | 1608 | *329* | 1279 | 0·26 |
| 0·27 | 68001 | *46716* | 21285 | *11028* | 10257 | *4242* | 6015 | *2066* | 3949 | *1159* | 2790 | *715* | 2075 | *471* | 1604 | *328* | 1276 | 0·27 |
| 0·28 | 66942 | *45844* | 21098 | *10903* | 10195 | *4208* | 5987 | *2053* | 3934 | *1153* | 2781 | *712* | 2069 | *469* | 1600 | *326* | 1274 | 0·28 |
| 0·29 | 65909 | *44994* | 20915 | *10782* | 10133 | *4174* | 5959 | *2040* | 3919 | *1147* | 2772 | *708* | 2064 | *468* | 1596 | *325* | 1271 | 0·29 |
| 0·30 | 64898 | *44165* | 20733 | *10662* | 10071 | *4139* | 5932 | *2028* | 3904 | *1141* | 2763 | *705* | 2058 | *466* | 1592 | *324* | 1268 | 0·30 |
| 0·31 | 63911 | *43357* | 20554 | *10543* | 10011 | *4106* | 5905 | *2015* | 3890 | *1135* | 2755 | *702* | 2053 | *465* | 1588 | *323* | 1265 | 0·31 |
| 0·32 | 62947 | *42570* | 20377 | *10427* | 9950 | *4073* | 5877 | *2002* | 3875 | *1129* | 2746 | *699* | 2047 | *463* | 1584 | *321* | 1263 | 0·32 |
| 0·33 | 62004 | *41801* | 20203 | *10312* | 9891 | *4041* | 5850 | *1989* | 3861 | *1124* | 2737 | *696* | 2041 | *461* | 1580 | *320* | 1260 | 0·33 |
| 0·34 | 61086 | *41055* | 20031 | *10199* | 9832 | *4009* | 5823 | *1977* | 3846 | *1117* | 2729 | *693* | 2036 | *459* | 1577 | *320* | 1257 | 0·34 |

| $\mu$ | 1 | $\Delta\nu$ | 2 | $\Delta\nu$ | 3 | $\Delta\nu$ | 4 | $\Delta\nu$ | 5 | $\Delta\nu$ | 6 | $\Delta\nu$ | 7 | $\Delta\nu$ | 8 | $\Delta\nu$ | 9 | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·35 | 60180 | *40320* | 19860 | *10087* | 9773 | *3977* | 5796 | *1964* | 3832 | *1112* | 2720 | *690* | 2030 | *457* | 1573 | *319* | 1254 | 0·35 |
| 0·36 | 59298 | *39606* | 19692 | *9977* | 9715 | *3945* | 5770 | *1952* | 3818 | *1106* | 2712 | *687* | 2025 | *455* | 1570 | *318* | 1252 | 0·36 |
| 0·37 | 58436 | *38910* | 19526 | *9869* | 9657 | *3914* | 5743 | *1940* | 3803 | *1100* | 2703 | *684* | 2019 | *453* | 1566 | *317* | 1249 | 0·37 |
| 0·38 | 57592 | *38229* | 19363 | *9763* | 9600 | *3883* | 5717 | *1928* | 3789 | *1094* | 2695 | *681* | 2014 | *452* | 1562 | *315* | 1247 | 0·38 |
| 0·39 | 56766 | *37564* | 19202 | *9658* | 9544 | *3853* | 5691 | *1916* | 3775 | *1098* | 2686 | *678* | 2008 | *450* | 1558 | *314* | 1244 | 0·39 |
| 0·40 | 55958 | *36916* | 19042 | *9554* | 9488 | *3823* | 5665 | *1904* | 3761 | *1083* | 2678 | *675* | 2003 | *449* | 1554 | *313* | 1241 | 0·40 |
| 0·41 | 55167 | *36283* | 18884 | *9452* | 9432 | *3793* | 5639 | *1892* | 3747 | *1078* | 2669 | *672* | 1997 | *447* | 1550 | *312* | 1238 | 0·41 |
| 0·42 | 54393 | *35665* | 18728 | *9351* | 9377 | *3763* | 5614 | *1880* | 3734 | *1073* | 2661 | *669* | 1992 | *445* | 1547 | *311* | 1236 | 0·42 |
| 0·43 | 53635 | *35061* | 18574 | *9252* | 9322 | *3733* | 5589 | *1869* | 3720 | *1067* | 2653 | *666* | 1987 | *444* | 1543 | *310* | 1233 | 0·43 |
| 0·44 | 52893 | *34471* | 18422 | *9154* | 9268 | *3704* | 5564 | *1857* | 3707 | *1062* | 2645 | *663* | 1982 | *442* | 1540 | *309* | 1231 | 0·44 |
| 0·45 | 52166 | *33894* | 18272 | *9057* | 9215 | *3676* | 5539 | *1846* | 3693 | *1057* | 2636 | *660* | 1976 | *440* | 1536 | *308* | 1228 | 0·45 |
| 0·46 | 51454 | *33330* | 18124 | *8962* | 9162 | *3648* | 5514 | *1835* | 3679 | *1051* | 2628 | *658* | 1970 | *438* | 1532 | *307* | 1225 | 0·46 |
| 0·47 | 50756 | *32778* | 17978 | *8869* | 9109 | *3620* | 5489 | *1823* | 3666 | *1046* | 2620 | *655* | 1965 | *436* | 1529 | *306* | 1223 | 0·47 |
| 0·48 | 50072 | *32239* | 17833 | *8776* | 9057 | *3592* | 5465 | *1812* | 3653 | *1041* | 2612 | *652* | 1960 | *435* | 1525 | *305* | 1220 | 0·48 |
| 0·49 | 49402 | *31712* | 17690 | *8685* | 9005 | *3565* | 5440 | *1801* | 3639 | *1035* | 2604 | *649* | 1955 | *433* | 1522 | *304* | 1218 | 0·49 |
| 0·50 | 48746 | *31197* | 17549 | *8596* | 8953 | *3537* | 5416 | *1790* | 3626 | *1030* | 2596 | *646* | 1950 | *432* | 1518 | *303* | 1215 | 0·50 |
| 0·51 | 48102 | *30693* | 17409 | *8507* | 8902 | *3510* | 5392 | *1779* | 3613 | *1025* | 2588 | *643* | 1945 | *430* | 1515 | *302* | 1213 | 0·51 |
| 0·52 | 47472 | *30201* | 17271 | *8419* | 8852 | *3484* | 5368 | *1769* | 3599 | *1019* | 2580 | *641* | 1939 | *428* | 1511 | *301* | 1210 | 0·52 |
| 0·53 | 46854 | *29719* | 17135 | *8333* | 8803 | *3457* | 5345 | *1759* | 3586 | *1014* | 2572 | *638* | 1934 | *427* | 1507 | *300* | 1207 | 0·53 |
| 0·54 | 46247 | *29247* | 17000 | *8248* | 8752 | *3431* | 5321 | *1748* | 3573 | *1009* | 2564 | *635* | 1929 | *425* | 1504 | *299* | 1205 | 0·54 |
| 0·55 | 45652 | *28785* | 16867 | *8164* | 8703 | *3405* | 5298 | *1737* | 3561 | *1004* | 2557 | *633* | 1924 | *424* | 1500 | *298* | 1202 | 0·55 |
| 0·56 | 45068 | *28332* | 16736 | *8082* | 8654 | *3379* | 5275 | *1727* | 3548 | *999* | 2549 | *630* | 1919 | *422* | 1497 | *297* | 1200 | 0·56 |
| 0·57 | 44496 | *27890* | 16606 | *8000* | 8606 | *3354* | 5252 | *1717* | 3535 | *994* | 2541 | *627* | 1914 | *421* | 1493 | *296* | 1197 | 0·57 |
| 0·58 | 43935 | *27458* | 16477 | *7919* | 8558 | *3329* | 5229 | *1707* | 3522 | *989* | 2533 | *624* | 1909 | *419* | 1490 | *295* | 1195 | 0·58 |
| 0·59 | 43384 | *27034* | 16350 | *7840* | 8510 | *3304* | 5206 | *1696* | 3510 | *984* | 2526 | *622* | 1904 | *418* | 1486 | *294* | 1192 | 0·59 |
| 0·60 | 42843 | *26618* | 16225 | *7762* | 8463 | *3280* | 5183 | *1686* | 3497 | *979* | 2518 | *619* | 1899 | *416* | 1483 | *293* | 1190 | 0·60 |
| 0·61 | 42313 | *26212* | 16101 | *7685* | 8416 | *3255* | 5161 | *1676* | 3485 | *975* | 2510 | *616* | 1894 | *414* | 1480 | *292* | 1188 | 0·61 |
| 0·62 | 41792 | *25814* | 15978 | *7608* | 8370 | *3231* | 5139 | *1666* | 3473 | *970* | 2503 | *614* | 1889 | *413* | 1476 | *291* | 1185 | 0·62 |
| 0·63 | 41281 | *25424* | 15857 | *7533* | 8324 | *3208* | 5116 | *1656* | 3460 | *965* | 2495 | *611* | 1884 | *411* | 1473 | *290* | 1183 | 0·63 |
| 0·64 | 40779 | *25042* | 15737 | *7459* | 8278 | *3184* | 5094 | *1646* | 3448 | *961* | 2487 | *608* | 1879 | *410* | 1469 | *289* | 1180 | 0·64 |
| 0·65 | 40286 | *24668* | 15618 | *7385* | 8233 | *3161* | 5072 | *1636* | 3436 | *956* | 2480 | *606* | 1874 | *408* | 1466 | *288* | 1178 | 0·65 |
| 0·66 | 39802 | *24301* | 15501 | *7313* | 8188 | *3137* | 5051 | *1627* | 3424 | *951* | 2473 | *604* | 1869 | *407* | 1462 | *287* | 1175 | 0·66 |
| 0·67 | 39327 | *23942* | 15385 | *7242* | 8143 | *3114* | 5029 | *1617* | 3412 | *947* | 2465 | *601* | 1864 | *405* | 1459 | *286* | 1173 | 0·67 |
| 0·68 | 38860 | *23589* | 15271 | *7172* | 8099 | *3091* | 5008 | *1608* | 3400 | *942* | 2458 | *598* | 1860 | *404* | 1456 | *285* | 1171 | 0·68 |
| 0·69 | 38401 | *23244* | 15157 | *7102* | 8055 | *3069* | 4986 | *1598* | 3388 | *937* | 2451 | *596* | 1855 | *403* | 1452 | *284* | 1168 | 0·69 |

TABLE III. (*continued.*)—*Rydberg's Interpolation Table* (*revised*).

Values of the Function $109678 \cdot 3/(m+\mu)^2$.

| $\mu$ | 1 | $\Delta\nu$ | 2 | $\Delta\nu$ | 3 | $\Delta\nu$ | 4 | $\Delta\nu$ | 5 | $\Delta\nu$ | 6 | $\Delta\nu$ | 7 | $\Delta\nu$ | 8 | $\Delta\nu$ | 9 | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·70 | 37951 | *22906* | 15045 | *7034* | 8011 | *3046* | 4965 | *1589* | 3376 | *933* | 2443 | *593* | 1850 | *401* | 1449 | *283* | 1166 | 0·70 |
| 0·71 | 37508 | *22574* | 14934 | *6966* | 7968 | *3024* | 4944 | *1580* | 3364 | *928* | 2436 | *591* | 1845 | *400* | 1445 | *282* | 1163 | 0·71 |
| 0·72 | 37074 | *22249* | 14825 | *6899* | 7926 | *3003* | 4923 | *1571* | 3352 | *923* | 2429 | *589* | 1840 | *398* | 1442 | *281* | 1161 | 0·72 |
| 0·73 | 36646 | *21930* | 14716 | *6833* | 7883 | *2981* | 4902 | *1562* | 3340 | *918* | 2422 | *586* | 1836 | *397* | 1439 | *280* | 1159 | 0·73 |
| 0·74 | 36226 | *21617* | 14609 | *6768* | 7841 | *2959* | 4882 | *1553* | 3329 | *915* | 2414 | *583* | 1831 | *395* | 1436 | *280* | 1156 | 0·74 |
| 0·75 | 35813 | *21310* | 14503 | *6704* | 7799 | *2938* | 4861 | *1544* | 3317 | *910* | 2407 | *581* | 1826 | *393* | 1433 | *279* | 1154 | 0·75 |
| 0·76 | 35408 | *21010* | 14398 | *6640* | 7758 | *2917* | 4841 | *1535* | 3306 | *906* | 2400 | *579* | 1821 | *392* | 1429 | *278* | 1151 | 0·76 |
| 0·77 | 35009 | *20815* | 14294 | *6577* | 7717 | *2897* | 4820 | *1526* | 3294 | *901* | 2393 | *576* | 1817 | *391* | 1426 | *277* | 1149 | 0·77 |
| 0·78 | 34616 | *20424* | 14192 | *6516* | 7676 | *2876* | 4800 | *1517* | 3283 | *897* | 2386 | *574* | 1812 | *389* | 1423 | *276* | 1147 | 0·78 |
| 0·79 | 34231 | *20141* | 14090 | *6454* | 7636 | *2856* | 4780 | *1508* | 3272 | *893* | 2379 | *572* | 1807 | *388* | 1419 | *275* | 1144 | 0·79 |
| 0·80 | 33851 | *19861* | 13990 | *6394* | 7596 | *2836* | 4760 | *1500* | 3260 | *888* | 2372 | *569* | 1803 | *387* | 1416 | *274* | 1142 | 0·80 |
| 0·81 | 33478 | *19588* | 13890 | *6334* | 7556 | *2815* | 4741 | *1492* | 3249 | *884* | 2365 | *567* | 1798 | *385* | 1413 | *273* | 1140 | 0·81 |
| 0·82 | 33111 | *19319* | 13792 | *6276* | 7516 | *2795* | 4721 | *1483* | 3238 | *880* | 2358 | *564* | 1794 | *384* | 1410 | *273* | 1137 | 0·82 |
| 0·83 | 32751 | *19056* | 13695 | *6218* | 7477 | *2776* | 4701 | *1474* | 3227 | *876* | 2351 | *562* | 1789 | *382* | 1407 | *272* | 1135 | 0·83 |
| 0·84 | 32396 | *18798* | 13598 | *6160* | 7438 | *2756* | 4682 | *1466* | 3216 | *872* | 2344 | *560* | 1784 | *380* | 1404 | *271* | 1133 | 0·84 |
| 0·85 | 32046 | *18543* | 13503 | *6104* | 7399 | *2736* | 4663 | *1458* | 3205 | *868* | 2337 | *557* | 1780 | *379* | 1401 | *270* | 1131 | 0·85 |
| 0·86 | 31703 | *18294* | 13409 | *6048* | 7361 | *2717* | 4644 | *1450* | 3194 | *864* | 2330 | *555* | 1775 | *378* | 1397 | *269* | 1128 | 0·86 |
| 0·87 | 31364 | *18048* | 13316 | *5993* | 7323 | *2698* | 4625 | *1442* | 3183 | *859* | 2324 | *553* | 1771 | *377* | 1394 | *268* | 1126 | 0·87 |
| 0·88 | 31032 | *17809* | 13223 | *5938* | 7285 | *2679* | 4606 | *1434* | 3172 | *855* | 2317 | *551* | 1766 | *375* | 1391 | *267* | 1124 | 0·88 |
| 0·89 | 30704 | *17572* | 13132 | *5884* | 7248 | *2661* | 4587 | *1425* | 3162 | *851* | 2311 | *549* | 1762 | *374* | 1388 | *267* | 1121 | 0·89 |
| 0·90 | 30382 | *17340* | 13042 | *5831* | 7211 | *2643* | 4568 | *1417* | 3151 | *847* | 2304 | *547* | 1757 | *372* | 1385 | *266* | 1119 | 0·90 |
| 0·91 | 30065 | *17113* | 12952 | *5778* | 7174 | *2625* | 4549 | *1409* | 3140 | *843* | 2297 | *544* | 1753 | *371* | 1382 | *265* | 1117 | 0·91 |
| 0·92 | 29752 | *16889* | 12863 | *5725* | 7138 | *2607* | 4531 | *1402* | 3129 | *839* | 2290 | *541* | 1749 | *370* | 1379 | *264* | 1115 | 0·92 |
| 0·93 | 29445 | *16669* | 12776 | *5674* | 7102 | *2589* | 4513 | *1394* | 3119 | *835* | 2284 | *540* | 1744 | *369* | 1375 | *263* | 1112 | 0·93 |
| 0·94 | 29142 | *16453* | 12689 | *5624* | 7065 | *2571* | 4494 | *1386* | 3108 | *831* | 2277 | *537* | 1740 | *368* | 1372 | *262* | 1110 | 0·94 |
| 0·95 | 28844 | *16241* | 12603 | *5573* | 7030 | *2554* | 4476 | *1378* | 3098 | *827* | 2271 | *535* | 1736 | *367* | 1369 | *261* | 1108 | 0·95 |
| 0·96 | 28550 | *16032* | 12518 | *5524* | 6994 | *2536* | 4458 | *1370* | 3088 | *824* | 2264 | *533* | 1731 | *365* | 1366 | *260* | 1106 | 0·96 |
| 0·97 | 28261 | *15827* | 12434 | *5475* | 6959 | *2519* | 4440 | *1363* | 3077 | *819* | 2258 | *531* | 1727 | *364* | 1363 | *260* | 1103 | 0·97 |
| 0·98 | 27976 | *15625* | 12351 | *5437* | 6924 | *2501* | 4423 | *1356* | 3067 | *816* | 2251 | *529* | 1722 | *362* | 1360 | *259* | 1101 | 0·98 |
| 0·99 | 27696 | *15428* | 12268 | *5379* | 6889 | *2484* | 4405 | *1348* | 3057 | *812* | 2245 | *527* | 1718 | *361* | 1357 | *258* | 1099 | 0·99 |
| 1·00 | 27420 | *15233* | 12187 | *5332* | 6855 | *2468* | 4387 | *1340* | 3047 | *809* | 2238 | *524* | 1714 | *360* | 1354 | *257* | 1097 | 1·00 |

# PART II.

# TABLES OF SERIES LINES.

# CHAPTER X.

## EXPLANATION OF TABLES.

The construction of the tables of spectra which follow may be gathered from the descriptions of series which have already been given, but a brief summary of the main points may not be superfluous.

The wave-number of a series line usually appears as the difference of two wave-numbers, one of which is the limit of the series to which it belongs. The lines of any one series are represented by the differences between the limit and a number of *terms* forming a *sequence*, the sequence being of the form $N/[f(m)]^2$, where $N$ is the Rydberg constant as determined from hydrogen, and $f(m)$ is of the form $m$ *plus* a fraction. The fractional part for successive lines is not constant, but varies with $m$, and the fraction may be represented approximately by the terms $(\mu+\alpha/m)$ of the Hicks formula, or by the corresponding terms of other formulæ.

When the limit of a series has been ascertained, the actual values of the terms of the sequence can be determined, independently of formulæ, by subtracting the wave-numbers of the observed lines from the wave-number representing the limit. Other terms of the sequence may be approximately calculated by the use of a formula when required.

The limit of a series appears as one of the terms of the sequence of another series. Thus the four chief series are represented by

| | | Limits. | | Terms. |
|---|---|---|---|---|
| $p(m)$ | = | $1s$ | — | $mp$ |
| $s(m)$ | = | $1p$ | — | $ms$ |
| $d(m)$ | = | $1p$ | — | $md$ |
| $f(m)$ | = | $2d$ | — | $mf$ |

As expressed in the combination principle, other series, or other lines, may appear corresponding to other combinations of terms from the various sequences; as $2s-mp$, $2p-mf$, and so on. For the analysis of a spectrum, whereby it is sought to associate as many lines as possible in a connected system, the terms of the four chief series are first determined, and afterwards utilised in a search for combinations. The procedure which has been adopted in recent years has accordingly been to rely upon formulæ mainly for the determination of the limit, or limits, of one of the chief series. The limits of the other chief series are then obtained by the aid of the Rydberg-Schuster and Runge laws, as illustrated on p. 24, and when these have been determined, the terms are derived by subtracting the wave-numbers of the observed lines from the respective limits.

In the tables, the wave-lengths, intensities, and wave-numbers of the observed lines of the four chief series are first given, followed by the separations in the case of doublets and triplets, and finally by the terms. Singlet, doublet and triplet series are distinguished respectively by capital, Greek and small letter abbreviations. Single lines which are derived by combination from doublet or triplet terms, however, are necessarily indicated by the symbols of the series from which they originate. Combinations cannot conveniently be represented by single letters, but their relations to the main series are readily shown by differences such as $2\delta-m\pi$, $1S-mp$, and so on.

The components of pairs and triplets, and the structure of members of the diffuse

series, are indicated by appropriate groupings of the lines. Unrecorded components or satellites are indicated, where necessary, by a dash (—). When two or more lines are available for the determination of a term the mean has been taken. When no intensity is stated it may usually be assumed, except for infra-red lines, that the intensity is low.

The wave-lengths from $\lambda 10000A$ to the ultra-violet are on the international scale unless otherwise stated. When the original determinations were on the Rowland scale they have been corrected by Table I. In the calculation of wave-numbers, the wave-lengths were corrected to vacuum by the Washington tables (Table II.) and the reciprocals taken.

Wave-lengths in the infra-red greater than $10000A$ are on Rowland's scale, unless otherwise stated, as the correction to the international system has only a slight effect on the wave-numbers. In view of the uncertainty as to the corrections to vacuum, the published wave-numbers have been adopted.

In the examples of formulæ which have been introduced, the series constant has been taken throughout as 109678·3, except for helium. Bohr's theory suggests a special value for each element, depending on the atomic weight (see p. 64), but the range is small, and the accuracy with which the lines are represented would scarcely be affected, if at all.

In the compilation of many of the tables, much assistance has been derived from reports on the admirable work carried on under the direction of Prof. Paschen which have been given by Dunz* and Lorenser.†

* B. Dunz, "Bearbeitung unserer Kenntnisse von den Serien." Dissertation, Tübingen (1911).

† E. Lorenser, "Beiträge zur Kenntnis der Bogenspektren der Erdalkalien." Dissertation, Tübingen (1913).

# CHAPTER XI.

## HYDROGEN AND HELIUM.

The spectra of hydrogen and helium have unusual features, and it will be convenient to refer to them apart from the general groups of elements.

### HYDROGEN.

H. At. wt.=1; At. No.=1.

In the vacuum tube spectrum of hydrogen there are usually two spectra superposed, one called the *primary* spectrum, which includes the Balmer series; and the other called the *secondary* spectrum, consisting of a great number of comparatively faint lines. The latter appears to consist, in part at least, of the components of a band spectrum, but it has not yet been completely analysed, and is not considered in the appended table.

The primary spectrum, as already explained (p. 14), does not form an ordinary system of series, but is represented closely by the formula

$$\nu=109678{\cdot}3\left(\frac{1}{m_1^2}-\frac{1}{m^2}\right)$$

When $m_1=1$, the formula gives lines in the Schumann region observed by Lyman; $m_1=2$ gives the Balmer series, and $m_1=3$ gives a series in the infra-red which was predicted by Ritz and partially observed by Paschen.

The lines of the Balmer series designated $H_\alpha$, $H_\beta$, are very close doublets, the separations in wave-length being respectively 0·14*A* and 0·08*A*, according to Michelson, the less refrangible components being the stronger. In a recent Paper, Merton* has described experiments on mixtures of hydrogen and helium, which show that each of these lines probably consists of three components, which exhibit great variations in their relative intensities under different conditions. The exact nature of these changes has not been completely determined, but the results are probably not inconsistent with Sommerfeld's theory of the fine structure of the lines.

Careful measurements of the first six lines of the Balmer series in an unresolved condition have been made by W. E. Curtis (p. 27), who found that the "centres of gravity" of the lines could not be represented within the limits of error by the simple formula given above.

The formula,

$$\nu=109678{\cdot}28\left[\frac{1}{(2-0{\cdot}00000383)^2}-\frac{1}{(m+0{\cdot}00000210)^2}\right]$$

was found by Curtis to represent the six observed lines with no error exceeding 0·001*A*, and the remaining lines with errors which probably do not exceed those of observation. The wave-lengths tabulated below have been calculated from this formula, and are the values in I.A. units (*i.e.*, in air at 15°C. and 760 mm.). In calculating the infra-red and ultra-violet series, it has been assumed that they may be regarded as combinations derived from terms of the Balmer series.

Paschen's wave-lengths† for the first four lines of the Balmer series are 6562·797,

* Proc. Roy. Soc., A. **97**, 307 (1920).
† Ann. d. Phys., **51**, No. 7 (1916).

4861·326, 4340·465, 4101·735. A discussion of these, in conjunction with Curtis's measures, has led H. Bell* to suggest 109677·9 as the value of the Rydberg constant $N$.

In an extension of Bohr's theory, J. Ishiwara† has given a formula for the hydrogen series which is written

$$\nu = N\left(\frac{1}{n_1^2-\sigma} - \frac{1}{n_2^2-\sigma}\right)$$

where the theoretical value of $\sigma = 3{\cdot}942 \times 10^{-5}$. From Curtis's wave-lengths for the first six lines of the Balmer series, Ishiwara found the mean value of $N$ to be 109678·05. The individual values (decimal parts) were 0·06, 0·01, 0·00, 0·04, 0·07, 0·10, showing an appreciably smaller range than those deduced from the simple Balmer formula.

H. BALMER SERIES.
Limit $= A = 27419{\cdot}674$.

| $m$ | $\lambda$, *I.A.* | $\nu$ | $A-\nu$ |
|---|---|---|---|
| 1 | — | — | 109677·82 |
| 2 | — | — | 27419·512 |
| 3 | 6562·793 | 15233·216 | 12186·458 |
| 4 | 4861·327 | 20564·793 | 6854·881 |
| 5 | 4340·466 | 23032·543 | 4387·131 |
| 6 | 4101·738 | 24373·055 | 3046·619 |
| 7 | 3970·075 | 25181·343 | 2238·331 |
| 8 | 3889·052 | 25705·957 | 1713·717 |
| 9 | 3835·387 | 26065·61 | 1354·06 |
| 10 | 3797·900 | 322·90 | 1096·77 |
| 11 | 70·633 | 513·24 | 906·43 |
| 12 | 50·154 | 658·03 | 761·64 |
| 13 | 34·371 | 770·68 | 648·99 |
| 14 | 21·941 | 860·09 | 559·58 |
| 15 | 11·973 | 932·21 | 487·46 |
| 16 | 03·855 | 991·24 | 428·43 |
| 17 | 3697·154 | 27040·16 | 379·51 |
| 18 | 91·557 | 81·16 | 338·51 |
| 19 | 86·834 | 27115·85 | 303·82 |
| 20 | 82·810 | 45·47 | 274·20 |
| 21 | 79·355 | 70·96 | 248·71 |
| 22 | 76·365 | 93·07 | 226·60 |
| 23 | 73·761 | 27212·35 | 207·32 |
| 24 | 71·478 | 29·26 | 190·41 |
| 25 | 69·466 | 44·19 | 175·48 |
| 26 | 67·684 | 57·42 | 162·25 |
| 27 | 66·097 | 69·23 | 150·44 |
| 28 | 64·679 | 79·78 | 139·89 |
| 29 | 63·405 | 89·26 | 130·41 |
| 30 | 62·258 | 97·81 | 121·86 |
| 31 | 61·221 | 27305·54 | 114·13 |
| 32 | 60·280 | 12·55 | 107·12 |
| 33 | 59·423 | 18·94 | 100·73 |
| 34 | 58·641 | 24·79 | 94·88 |
| 35 | 57·926 | 30·14 | 89·53 |
| 36 | 57·269 | 35·05 | 84·62 |
| 37 | 56·666 | 39·55 | 80·12 |
| ∞ | 45·981 | 27419·674 | 0 |

H. INFRA-RED SERIES.
Limit $= A = 12186{\cdot}46$.

| $m$ | $\lambda$ air. | $\lambda$ vac. | $\nu$ | $A-\nu$ |
|---|---|---|---|---|
| 4 | 18751·05 | 18756·17 | 5331·58 | 6854·88 |
| 5 | 12818·11 | 12821·61 | 7799·33 | 4387·13 |

Paschen's observed values, on Rowland's scale, are 18751·3, 12817·6; these give $\nu_4 = 5331{\cdot}53$ and $\nu_5 = 7799{\cdot}67$.

H. ULTRA-VIOLET SERIES.
Limit $= A = 109677{\cdot}82$.

| $m$ | $\lambda$ vac. | $\nu$ | $A-\nu$ |
|---|---|---|---|
| 2 | 1215·68 | 82258·31 | 27419·51 |
| 3 | 1025·83 | 97481·36 | 12186·46 |
| 4 | 972·54 | 102822·94 | 6854·88 |

The wave-lengths, in vacuo, as observed by Lyman, are 1216·0, 1026·0, 972·7.

Millikan finds 1215·7 for the first line.

NOTE.—The provisional wave-lengths given by Wood for the nine lines of the Balmer series first observed by him in the laboratory spectrum are as follows:—

| $\lambda$ *R.* | | $\lambda$ *I.A.* |
|---|---|---|
| 3722·12 | ... | 3721·97 |
| 12·22 | ... | 12·07 |
| 03·92 | ... | 03·77 |
| 3697·35 | ... | 3697·20 |
| 91·72 | ... | 91·57 |
| 86·99 | ... | 86·84 |
| 82·96 | ... | 82·81 |
| 79·46 | ... | 79·31 |
| 3676·44 | ... | 76·29 |

* Phil. Mag., **40**, 489 (1920).

† Math. & Phys. Soc., Tokyo, Series 2, **8**, 179 (1915).

## HELIUM.

He. At. wt. = 4 ; At. No. = 2.

The line spectrum of helium, as observed ordinarily in vacuum tubes, consists of a system of singlet series and a system of doublets. The doublets are very close, the wave-number separation being about 1·02, so that in the principal series only the first member has been resolved, and only the earlier members of the sharp and diffuse series. The doublets are somewhat unusual, inasmuch as in the sharp and diffuse series the stronger component is on the more refrangible side, while the first principal line has its stronger component on the side of greater wave-length. The weaker components are also unusually faint in comparison with the chief lines.

The majority of the measurements are by Runge and Paschen,* but the more recent interferometer values determined by Merrill at the Bureau of Standards, Washington,† have been substituted for 21 lines ; the greatest error in these values is believed not to exceed 0·003 *A*. In the case of doublets, the Washington values refer to the stronger components, and the wave-lengths of the companion lines have been adjusted to show the same separations as those indicated by Runge and Paschen's values. The infra-red wave-lengths are by Paschen.‡ The last two lines in the principal series of doublets are due to Schniederjost.§

It should be noted that the resolution of the spectrum into two systems of series was regarded by some as indicating the presence of two gases, which were distinguished as helium and parhelium, giving the doublet and singlet systems respectively. There is now no reason to believe that helium is other than a single element, but the name "parhelium" has to some extent survived. In connection with his work on stellar spectra, Lockyer re-named this pseudo-element "asterium." The doublet and singlet systems are also sometimes distinguished as He I. and He II. respectively.

The following Hicks formula has been calculated from the three lines of the sharp series of singlets measured at Washington :—

$$S(m)=27175{\cdot}17-\frac{109723{\cdot}2}{\left(m+0{\cdot}862157-\frac{0{\cdot}010908}{m}\right)^2}$$

As will be seen from the following list of the differences "observed *minus* calculated" wave-numbers, the formula represents all but the first line with considerable accuracy. Lines marked with an asterisk were used in the calculation of constants.

| $m$ | $O-C$ ($\Delta\nu$) | $m$ | $O-C$ ($\Delta\nu$) | $m$ | $O-C$ ($\Delta\nu$) |
|---|---|---|---|---|---|
| 1 | −16·4 | 5 | +0·10 | 9 | +0·49 |
| 2 | 0·00* | 6 | +0·14 | 10 | not observed. |
| 3 | 0·00* | 7 | +0·52 | 11 | −0·02 |
| 4 | 0·00* | 8 | +0·35 | 12 | +1·85 |

The later lines were probably less accurately measured than the earlier ones in consequence of their low intensities.

For the doublet system, the following formula for the stronger components of

* Astrophys. Jour., **3**, 4 (1896).
† Astrophys. Jour., **46**, 357 (1917).
‡ Ann. d. Phys., **27**, 537 (1908) ; **29**, 628 (1909).
§ Zeit. f. Wiss. Phot., **2**, 265 (1904).

the diffuse series has been calculated from the first, third and fifth lines as measured at Washington :—

$$\delta_1(m)=29223{\cdot}88-\frac{109723{\cdot}2}{\left(m+0{\cdot}996982+\frac{0{\cdot}001695}{m}\right)^2}$$

giving the following residuals :—

| $m$ | $O-C(\Delta\nu)$ | $m$ | $O-C(\Delta\nu)$ | $m$ | $O-C(\Delta\nu)$ |
|---|---|---|---|---|---|
| 2 | +0·02* | 8 | —0·08 | 14 | +0·08 |
| 3 | —0·06 | 9 | —0·22 | 15 | +0·33 |
| 4 | 0·00* | 10 | —0·08 | 16 | +0·30 |
| 5 | +0·02 | 11 | +0·09 | 17 | —1·7 ? |
| 6 | 0·00* | 12 | +0·13 | 18 | +1·2 |
| 7 | 0·00 | 13 | +0·01 | | |

The limits of other main series were deduced by the application of the Rydberg-Schuster and Runge laws. All the observed lines are either included in the main series of singlets or doublets or are accounted for as combinations.

Several combination series are observed in the helium spectrum when the gas is subjected to strong electric fields. The first of these was recorded by Koch,* and others have been observed by Merton,† Stark‡ and Liebert.§ The wave-lengths of most of these lines have only been roughly measured, and the wave-lengths calculated from the combinations have therefore been inserted in the tables for comparison with the observations.

Besides the line spectrum, there is an interesting band spectrum of helium, which is well developed under appropriate experimental conditions.|| It was found by Fowler¶ that the heads of some of the stronger bands, in contrast with all other known band spectra, are arranged in accordance with the laws of line-series. There is, however, no apparent relation between the band- and line-series, except that the main series of bands runs nearly parallel to the principal series of helium doublets. Thus, a displacement of the latter towards the red by a wave-number interval of 4159 would nearly superpose it on the stronger heads of the main set of bands.

## Ionised Helium ($He^+$).

Under the action of strong discharges, as already mentioned ,helium yields another system of lines for which the series constant has rather more than four times the value deduced from hydrogen. Otherwise the series resemble those of hydrogen, and can be represented closely by an equally simple formula, namely,

$$\nu=4N'\left(\frac{1}{m_1^2}-\frac{1}{m^2}\right)$$

where $N'$ has the value 109723·22 as compared with 109678·3 for hydrogen.

* Ann. d. Phys., **48**, 98 (1915).
† Proc. Roy. Soc., A. **95**, 30 (1918).
‡ Ann. d. Phys., **56**, 577 (1918).
§ Ann. d. Phys., **56**, 600-617 (1918).
|| W. E. Curtis, Proc. Roy. Soc., A. **89**, 146 (1913). E. Goldstein, Verh. d. Deutsch. Phys. Gesell., **15**, 402 (1913).
¶ Proc. Roy. Soc., A. **91**, 208 (1915).

## Helium, Doublet System.

**Principal. $1\sigma - m\pi$.**
$1\sigma = 38454{\cdot}71$.

| λ, Int. | ν | Δν | m | $m\pi_{2,1}$ |
|---|---|---|---|---|
| *10829·09 } (200) | 9231·86 | 1·03 | (1) | 29222·85 |
| *10830·30 } | 9230·83 | | | 29223·88 |
| †3888·646 (10) | 25708·63 | | (2) | 12746·08 |
| †3187·743 (8) | 31361·12 | | (3) | 7093·59 |
| †2945·104 (6) | 33944·75 | | (4) | 4509·96 |
| 2829·06 (4) | 35337·05 | | (5) | 3117·66 |
| 2763·80 (2) | 36171·40 | | (6) | 2283·31 |
| 2723·18 (1) | 36710·92 | | (7) | 1743·79 |
| 2696·13 (1) | 37079·21 | | (8) | 1375·50 |
| 2677·1 (1) | 37342·7 | | (9) | 1112·0 |
| 2663·2 (1) | 37537·5 | | (10) | 917·2 |
| 2652·95 | 37682·67 | | (11) | 772·04 |
| 2644·84 | 37798·22 | | (12) | 656·49 |

**Sharp. $1\pi - m\sigma$.**
$1\pi_2 = 29222{\cdot}85$ ; $1\pi_1 = 29223{\cdot}88$.

| λ, Int. | ν | Δν | m | mσ |
|---|---|---|---|---|
| —10829·09 } (200) | — 9231·86 | 1·03 | (1) | 38454·71 |
| —10830·10 } | — 9230·83 | | | |
| 7065·677 (1) | 14149·03 | 0·98 | (2) | 15073·87 |
| †7065·185 (5) | 14150·01 | | | |
| 4713·366 (1) | 21210·34 | 1·01 | (3) | 8012·53 |
| †4713·143 (3) | 21211·35 | | | |
| 4120·981 (1) | 24259·24 | 1·01 | (4) | 4963·63 |
| †4120·812 (3) | 24260·25 | | | |
| 3867·62 (1) | 25848·40 | 1·06 | (5) | 3374·42 |
| 3867·46 (2) | 25849·46 | | | |
| 3732·99 (1) | 26780·58 | 1·01 | (6) | 2442·29 |
| 3732·85 (1) | 26781·59 | | | |
| 3652·12 (1) | 27373·58 | 0·90 | (7) | 1849·40 |
| 3652·00 (1) | 27374·48 | | | |
| 3599·46 (1) | 27774·05 | 1·06 | (8) | 1448·77 |
| 3599·32 (1) | 27775·11 | | | |
| 3562·98 (1) | 28058·41 | | (9) | 1165·47 |
| 3536·81 (1) | 28265·96 | | (10) | 957·92 |
| 3517·33 (1) | 28422·56 | | (11) | 801·32 |
| 3502·32 (1) | 28544·37 | | (12) | 679·51 |
| 3490·62 (1) | 28640·04 | | (13) | 583·84 |
| 3481·4 | 28715·8 | | (14) | 508·1 |

**Diffuse. $1\pi - m\delta$.**
$1\pi_2 = 29222{\cdot}85$ ; $1\pi_1 = 29223{\cdot}88$.

| λ, Int. | ν | Δν | m | mδ |
|---|---|---|---|---|
| 5875·960 (1) | 17013·79 | 0·99 | (2) | 12209·10 |
| †5875·618 (10) | 17014·78 | | | |
| 4471·689 (1) | 22356·66 | 1·06 | (3) | 6866·16 |
| †4471·477 (6) | 22357·72 | | | |
| 4026·358 (1) | 24829·34 | 1·05 | (4) | 4393·49 |
| †4026·189 (5) | 24830·39 | | | |
| 3819·753 (1) | 26172·30 | 1·01 | (5) | 3050·57 |
| †3819·606 (4) | 26173·31 | | | |
| 3705·139 (1) | 26981·90 | 0·98 | (6) | 2241·00 |
| †3705·003 (3) | 26982·88 | | | |
| 3634·37 (1) | 27507·27 | 0·99 | (7) | 1715·62 |
| 3634·24 (2) | 27508·26 | | | |
| 3587·42 (1) | 27867·26 | 1·09 | (8) | 1355·53 |
| 3587·28 (2) | 27868·35 | | | |
| 3554·57 (1) | 28124·79 | 1·02 | (9) | 1098·07 |
| 3554·44 (1) | 28125·81 | | | |
| 3530·50 (1) | 28316·53 | | (10) | 907·35 |
| 3512·50 (1) | 28461·64 | | (11) | 762·24 |
| 3498·63 (1) | 28574·47 | | (12) | 649·41 |
| 3487·72 (1) | 28663·85 | | (13) | 560·03 |
| 3478·95 (1) | 28736·11 | | (14) | 487·77 |
| 3471·78 (1) | 28795·45 | | (15) | 428·43 |
| 3465·89 (1) | 28844·39 | | (16) | 379·49 |
| 3461·2 ? (1) | 28883·4 | | (17) | 340·5 |
| 3456·7 (1) | 28921·0 | | (18) | 302·9 |

**Fundamental. $2\delta - m\varphi$.**
$2\delta = 12209{\cdot}10$.

| λ, Int. | ν | Δν | m | mφ |
|---|---|---|---|---|
| 18684·2 (3) | 5350·71 | | (3) | 6858·39 |
| 12784·6 (1) | 7819·89 | | (4) | 4389·21 |

* Measures in I.A. (Paschen). λ 10830 is the chief component.

† Interferometer measures, Bureau of Standards, Washington.

## HELIUM, DOUBLET SYSTEM—*Continued.*

### COMBINATIONS.

| λ obs. | ν | ν calc. |
|---|---|---|
| 17002·55 | 5879·87 | $2\pi_1-3\delta=5879\cdot92$ |
| | λ calc. | |
| *3809·05 | 3809·08 | $1\sigma-2\delta=26245\cdot61$ |
| *3166 | 3164·79 | $1\sigma-3\delta=31588\cdot55$ |
| *2936 | 2935·03 | $1\sigma-4\delta=34061\cdot22$ |
| *2824 | 2823·70 | $1\sigma-5\delta=35404\cdot14$ |
| *2761 | 2760·57 | $1\sigma-6\delta=36213\cdot71$ |
| *2722 | 2721·09 | $1\sigma-7\delta=36739\cdot09$ |
| ‡6059·8 | 6067·09 | $1\pi_1-2\pi=16477\cdot80$ |
| ‡4518·59 | 4517·43 | $1\pi_1-3\pi=22130\cdot29$ |
| ‡4045·87 | 4045·16 | $1\pi_1-4\pi=24713\cdot92$ |
| ‡3829·85 | 3829·42 | $1\pi_1-5\pi=26106\cdot22$ |
| ‡3711·15 | 3710·85 | $1\pi_1-6\pi=26940\cdot57$ |
| ‡3636·75 | 3637·96 | $1\pi_1-7\pi=27480\cdot09$ |

| λ obs. | λ calc. | ν calc. |
|---|---|---|
| ‡ 3586·55 | 3589·85 | $1\pi_1-8\pi=27848\cdot38$ |
| ... | 4275·81 | $1\sigma-2\sigma=23380\cdot84$ |
| ... | 3283·97 | $1\sigma-3\sigma=30442\cdot18$ |
| †2986 | 2985·00 | $1\sigma-4\sigma=33491\cdot08$ |
| †2851 | 2849·77 | $1\sigma-5\sigma=35080\cdot29$ |
| †2777 | 2776·00 | $1\sigma-6\sigma=36012\cdot42$ |
| †2732 | 2731·04 | $1\sigma-7\sigma=36605\cdot31$ |

* Stark's "diffuse principal" series; λ 3809 previously observed by Paschen.

† Stark's "sharp principal" series.

‡ Stark's "near sharp" (fastscharfe) series; measures by Liebert. Koch's "third subordinate" series.

## HELIUM, SINGLET SYSTEM.

### PRINCIPAL. $1S-mP$. $1S=32032\cdot51$.

| λ, Int. | ν | m | mP |
|---|---|---|---|
| 20582·04 (20) | 4857·34 | (1) | 27175·17 |
| † 5015·675 (6) | 19931·95 | (2) | 12100·56 |
| † 3964·727 (4) | 25215·30 | (3) | 6817·21 |
| † 3613·641 (3) | 27665·06 | (4) | 4367·45 |
| 3447·594 (2) | 28997·46 | (5) | 3035·05 |
| 3354·52 (1) | 29801·99 | (6) | 2230·52 |
| 3296·76 (1) | 30324·11 | (7) | 1708·40 |
| 3258·30 (1) | 30682·04 | (8) | 1350·47 |
| 3231·20 (1) | 30939·35 | (9) | 1093·16 |
| 3211·50 (1) | 31129·13 | (10) | 903·38 |
| 3196·68 (1) | 31273·45 | (11) | 759·06 |
| ... | ... | (12) | ... |
| 3176·5? (1) | 31472·4 | (13) | 560·1 |

### SHARP. $1P-mS$. $1P=27175\cdot17$.

| λ, Int. | ν | m | mS |
|---|---|---|---|
| —20582·04 (20) | —4857·34 | (1) | 32032·51 |
| † 7281·349 (3) | 13729·94 | (2) | 13445·23 |
| † 5047·736 (2) | 19805·35 | (3) | 7369·82 |
| † 4437·549 (1) | 22528·65 | (4) | 4646·52 |
| 4168·97 (1) | 23980·00 | (5) | 3195·17 |
| 4023·99 (1) | 24843·96 | (6) | 2331·21 |
| 3935·91 (1) | 25399·92 | (7) | 1775·25 |
| 3878·18 (1) | 25778·02 | (8) | 1397·15 |
| 3838·09 (1) | 26047·26 | (9) | 1127·91 |
| ... | ... | (10) | 930·15 |
| 3787·49 (1) | 26395·24 | (11) | 779·93 |
| 3770·57 (1) | 26513·69 | (12) | 661·48 |

### FUNDAMENTAL. $2D-mF$. $2D=12205\cdot1$.

| λ, Int. | ν | m | mF |
|---|---|---|---|
| 18693·4 (2) | 5348·0 | (3) | 6857·1 |
| 12792·2 (1) | 7815·1 | (4) | 4390·0 |

† Interferometer measures, Bureau of Standards, Washington.

### DIFFUSE. $1P-mD$. $1P=27175\cdot17$.

| λ, Int. | ν | m | mD |
|---|---|---|---|
| † 6678·149 (6) | 14970·08 | (2) | 12205·09 |
| † 4921·929 (4) | 20311·57 | (3) | 6863·60 |
| † 4387·928 (3) | 22783·41 | (4) | 4391·76 |
| 4143·77 (2) | 24125·84 | (5) | 3049·33 |
| 4009·27 (1) | 24935·17 | (6) | 2240·00 |
| 3926·53 (1) | 25460·59 | (7) | 1714·58 |
| 3871·80 (1) | 25820·49 | (8) | 1354·68 |
| 3833·56 (1) | 26078·04 | (9) | 1097·13 |
| 3805·75 (1) | 26268·60 | (10) | 906·57 |
| 3784·88 (1) | 26413·44 | (11) | 761·73 |
| 3768·80 (1) | 26526·14 | (12) | 649·03 |
| 3756·09 (1) | 26615·88 | (13) | 559·29 |

### COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 19090·58 | 5236·78 | $2P-3D=5236\cdot96$ |
| λ obs. | λ calc. | |
| § 6635 | 6631·84 | $1P-2P=15074\cdot61$ |
| § 4910·6 | 4910·61 | $1P-3P=20357\cdot96$ |
| § 4384·3 | 4383·25 | $1P-4P=22807\cdot72$ |
| § 4143·2 | 4141·32 | $1P-5P=24140\cdot12$ |
| ‡ ... | 5378·59 | $1S-2S=18587\cdot28$ |
| ‡ ... | 4053·56 | $1S-3S=24662\cdot69$ |
| ‡ ... | 3650·46 | $1S-4S=27385\cdot99$ |
| ‡ 3468 | 3466·74 | $1S-5S=28837\cdot34$ |
| * 5043 | 5042·15 | $1S-2D=19827\cdot42$ |
| ‖ 3974 | 3972·04 | $1S-3D=25168\cdot91$ |
| ‖ 3618 | 3616·82 | $1S-4D=27640\cdot75$ |
| ‖ 3450 | 3449·29 | $1S-5D=28983\cdot18$ |
| ‖ 3356 | 3355·59 | $1S-6D=29792\cdot51$ |

* Merton, Proc. Roy. Soc., A. **98**, 258 (1920).

‡ Stark's "sharp-principal" series.

§ Observed by Merton, Stark, and Liebert.

‖ Stark's "diffuse-principal" series.

$m_1=3$ gives a strong series of which $\lambda 4686$ is the first member, and of which seven lines were observed; $m_1=4$ gives a fainter series with several lines in the visible spectrum, including the "Pickering lines"; and $m_1=2$ gives a series in the Schumann region, of which two members have been observed by Lyman.* There was at first some confusion as to the origin of these lines, but they may now be certainly attributed to ionised helium (p. 62).

The fine structure of these lines has been studied by Paschen.† Wave-lengths of the lines have been determined by Fowler, Evans,‡ and Paschen, as in the following table. The values of Fowler and Evans have been corrected to the international scale, and those of Paschen are for the chief components of the complex lines observed by him. Paschen's values are entitled to greatest weight.

| Fowler. | Paschen. | Fowler. | Evans. | Paschen. | Lyman. |
|---|---|---|---|---|---|
| 4685·81 | 4685·808 | | 6560·21 | 6560·130 | |
| 3203·17 | 3203·165 | 5410·29 | 5411·67 | 5411·551 | 1640·2 |
| 2733·24 | 2733·345 | | | 4859·342 | 1215·1 |
| 2511·22 | 2511·249 | 4541·13 | 4541·72 | 4541·612 | |
| 2385·39 | 2385·440 | | 4339·81 | 4338·694 | |
| 2306·12 | 2306·215 | 4200·14 | 4199·79 | 4199·857 | |
| 2252·81 | ..... | | | 4100·049 | |

The values tabulated below have been calculated from the general formula, $m$ being given integral values, and the constant $4N'$ having been calculated from the observed line 4685·81.

He+ (Calculated Values).

"4686" Series.

$$\nu=4\times 109723{\cdot}22\left(\frac{1}{3^2}-\frac{1}{m^2}\right)$$

Limit $=A=48765{\cdot}87$.

| λ, *I.A.*(air). | ν | m | A—ν |
|---|---|---|---|
| 4685·81 | 21335·07 | (4) | 27430·80 |
| 3203·16 | 31210·16 | (5) | 17555·71 |
| 2733·34 | 36574·40 | (6) | 12191·47 |
| 2511·25 | 39808·87 | (7) | 8957·00 |
| 2385·46 | 41908·17 | (8) | 6857·70 |
| 2306·18 | 43347·44 | (9) | 5418·43 |
| 2252·72 | 44376·94 | (10) | 4388·93 |

"Lyman" Series.

$$\nu=4\times 109723{\cdot}22\left(\frac{1}{2^2}-\frac{1}{m^2}\right)$$

Limit $=109723{\cdot}22$.

| λ, *I.A.*vac. | ν | m | A—ν |
|---|---|---|---|
| 1640·49 | 60957·35 | (3) | 48765·87 |
| 1215·18 | 82292·42 | (4) | 27430·80 |
| 1084·98 | 92167·51 | (5) | 17555·71 |
| 921·39 | 108531·75 | (6) | 12191·47 |

"Pickering" Series.*

$$\nu=4\times 109723{\cdot}22\left(\frac{1}{4^2}-\frac{1}{m^2}\right)$$

Limit $=27430{\cdot}80$.

| λ, *I.A.*(air). | ν | m | A—ν |
|---|---|---|---|
| 10123·72 | 9875·09 | (5) | 17555·71 |
| 6560·16 | 15239·33 | (6) | 12191·47 |
| 5411·57 | 18473·80 | (7) | 8957·00 |
| 4859·36 | 20573·10 | (8) | 6857·70 |
| 4541·63 | 22012·37 | (9) | 5418·43 |
| 4338·71 | 23041·87 | (10) | 4388·93 |
| 4199·87 | 23803·59 | (11) | 3627·21 |
| 4100·08 | 24382·93 | (12) | 3047·87 |
| 4025·64 | 24833·80 | (13) | 2597·00 |
| 3968·47 | 25191·75 | (14) | 2239·25 |
| 3923·51 | 25480·17 | (15) | 1950·63 |
| 3887·47 | 25716·38 | (16) | 1714·42 |
| 3858·10 | 912·14 | (17) | 1518·66 |
| 3833·83 | 26076·19 | (18) | 1354·61 |
| 3813·53 | 215·03 | (19) | 1215·77 |
| 3796·36 | 333·57 | (20) | 1097·23 |
| 3781·71 | 435·58 | (21) | 995·22 |

* The original "Pickering" or "ζ Puppis" series included only alternate lines, beginning with 5411.

* Nature, **104**, 314, 565 (1919).
† Ann. d. Phys., **50**, 901 (1916).
‡ Phil. Mag., **29**, 284 (1915).

# CHAPTER XII.

## GROUP IA.—THE ALKALI METALS.

The chief series in the arc spectra of the alkali metals consist of doublets, the separations of which increase with the atomic weight. There is also a general displacement of corresponding series in the different elements towards the red as the atomic weight increases. Lines of the principal series are easily reversed, and were traced towards their limits by Bevan* in his experiments on the absorption of the metallic vapours.

The allotment of the lines to the respective series is essentially as given by Dunz in his Tübingen dissertation. In the principal series, the first pair appears with + sign in all the metals of the group, and the limits of the sharp and diffuse series consequently lie on the red side of the limits of the respective principal series. The fundamental series lie still further to the red.

The numeration of the diffuse series, following Rydberg, is based upon potassium, in which case the sharp and diffuse series are nearly coincident and the adjacent members have been assigned the same numbers. There are then no lines with order-number less than 2 in the diffuse series, negative members corresponding to the order-number 1 not having been recorded.

In the Rydberg formulæ for the principal series, $\mu$ is $>1$ except in the case of lithium ; in the sharp and diffuse series $\mu$ is always $<1$. In the fundamental series the order-numbers have been chosen so as to make $\mu$ nearly unity.

References to sources of data are given in connection with each element, but to avoid repetition it may be stated that the observations of Meggers† and Meissner‡ in the red have been utilised as far as possible.

Enhanced lines have been observed in each of the elements except lithium, but no series have yet been identified.

### LITHIUM.

Li. At. wt.=7·0 ; At. No.=3.

The arc spectrum of lithium is characterised by well-marked series, of which the principal has the first line in the red and the other members in the ultra-violet, whilst the brighter parts of the subordinate series are in the visible region, and the fundamental series in the infra-red. The system consists of close doublets, as in the other alkali metals ; but in the ordinary arc they are very diffuse, so that the components are not separated except in the case of the first principal line. In vacuum tubes, however, five of the lines have been resolved into their components by N. A. Kent,§ who made use of a powerful echelon grating. Kent's results are as follows :—

| $\lambda$ | $\Delta\lambda$ | $\Delta\nu$ | Series |
|---|---|---|---|
| 8126 | 0·225*A* | 0·340 | $\sigma$ |
| 6708 | 0·151 | 0·336 | $\pi$ |
| 6103 | 0·115 | 0·309 | $\delta$ |
| 4972 | 0·084 | 0·339 | $\sigma$ |
| 4603 | 0·070 | 0·328 | $\delta$ |

* Proc. Roy. Soc., A. **83**, 421 (1910) ; **85**, 54 (1911) ; **86**, 320 (1912).
† Scientific Papers, Bureau of Standards, Washington, No. 312 (1918).
‡ Ann. d. Phys., **50**, 713 (1916).
§ Astrophys. Jour., **40**, 337 (1914).

## LITHIUM.

PRINCIPAL. $1\sigma - m\pi$.
$1\sigma = 43486{\cdot}3$.

| λ, Int. | ν | m | mπ |
|---|---|---|---|
| 6707·85 (10*R*) | 14903·8 | (1) | 28582·5 |
| 3232·61 (8*R*) | 30925·9 | (2) | 12560·4 |
| 2741·31 (6*R*) | 36468·1 | (3) | 7018·2 |
| 2562·50 (5*R*) | 39012·7 | (4) | 4473·6 |
| 2475·29 (4*R*) | 40387·1 | (5) | 3099·2 |
| 2425·68 (3*R*) | 41213·0 | (6) | 2273·3 |
| 2394·48 (1*R*) | 41750·0 | (7) | 1736·3 |
| 73·8 | 42113·6 | (8) | 1372·7 |
| 59·3 | 372·7 | (9) | 1113·6 |
| 48·4 | 569·1 | (10) | 917·2 |
| 40·4 | 714·6 | (11) | 771·7 |
| 34·2 | 828·0 | (12) | 658·3 |
| 28·9 | 925·6 | (13) | 560·7 |
| 25·1 | 995·6 | (14) | 490·7 |
| 21·8 | 43056·9 | (15) | 429·4 |
| 19·2 | 105·1 | (16) | 381·2 |
| 17·0 | 146·0 | (17) | 340·3 |
| 15·1 | 181·4 | (18) | 304·9 |
| 13·5 | 211·3 | (19) | 275·0 |
| 12·1 | 237·4 | (20) | 248·9 |
| 11·0 | 258·0 | (21) | 228·3 |
| 09·9 | 276·4 | (22) | 209·9 |
| 08·9 | 297·4 | (23) | 188·9 |
| 08·2 | 310·5 | (24) | 175·8 |
| 07·4 | 325·5 | (25) | 160·8 |
| 06·82 | 336·4 | (26) | 149·9 |
| 06·40 | 344·3 | (27) | 142·0 |
| 05·82 | 355·2 | (28) | 131·1 |
| 05·36 | 363·8 | (29) | 122·5 |
| 04·94 | 371·7 | (30) | 114·6 |
| 04·58 | 378·5 | (31) | 107·8 |
| 04·24 | 384·9 | (32) | 101·4 |
| 03·95 | 391·3 | (33) | 95·0 |
| 03·68 | 395·4 | (34) | 90·9 |
| 03·41 | 400·5 | (35) | 85·8 |
| 03·19 | 404·7 | (36) | 81·6 |
| 02·98 | 408·6 | (37) | 77·7 |
| 02·78 | 412·4 | (38) | 73·9 |
| 02·54 | 416·9 | (39) | 69·4 |
| 02·33 | 420·9 | (40) | 65·4 |
| 02·15 | 424·3 | (41) | 62·0 |

SHARP. $1\pi - m\sigma$.
$1\pi = 28582{\cdot}5$.

| λ, Int. | ν | m | mσ |
|---|---|---|---|
| —6707·85 (10*R*) | —14903·8 | (1) | 43486·3 |
| 8126·52 (10) | 12302·0 | (2) | 16280·5 |
| 4971·93 (7*r*) | 20107·3 | (3) | 8475·2 |
| 4273·28 (5*r*) | 23394·7 | (4) | 5187·8 |
| 3985·79 (3*r*) | 25082·1 | (5) | 3500·4 |
| *3838·15 (1*r*) | 26046·9 | (6) | 2535·6 |

* There is some doubt about these lines.

DIFFUSE. $1\pi - m\delta$.
$1\pi = 28582{\cdot}5$.

| λ, Int. | ν | m | mδ |
|---|---|---|---|
| 6103·53 (10*R*) | 16379·4 | (2) | 12203·1 |
| 4602·99 (9*R*) | 21719·0 | (3) | 6863·5 |
| 4132·29 (8) | 24192·9 | (4) | 4389·6 |
| 3915·0 (6) | 25535·5 | (5) | 3047·0 |
| 3794·7 (5) | 26345·1 | (6) | 2237·4 |
| 3718·7 (3) | 26883·5 | (7) | 1699·0 |
| 3670·4 (1) | 27237·3 | (8) | 1345·2 |

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 12203{\cdot}1$

| λ | ν | m | mφ |
|---|---|---|---|
| 18697·0 | 5347·0 | (3) | 6856·1 |
| 12782·2 | 7821·3 | (4) | 4381·8 |

COMBINATION. $1\pi - m\pi$.
$1\pi = 28582{\cdot}5$

| λ | ν | m | ν calc. |
|---|---|---|---|
| 6240·1 | 16021·0 | (2) | 16022·1 |
| 4636·1 | 21563·9 | (3) | 21564·3 |
| 4148·0 | 24101·2 | (4) | 24108·9 |
| *3921·65 | 25492·3 | (5) | 25483·3 |

COMBINATION. $2\pi - m\sigma$.
$2\pi = 12560{\cdot}4$.

| λ | ν | m | ν calc. |
|---|---|---|---|
| 24467·0 | 4086·1 | (3) | 4085·2 |
| 13566·4 | 7369·5 | (4) | 7372·6 |

COMBINATION. $2\pi - m\delta$.
$2\pi = 12560{\cdot}4$.

| λ | ν | m | ν calc. |
|---|---|---|---|
| 17551·6 | 5696·0 | (3) | 5696·9 |
| 12232·4 | 8172·8 | (4) | 8170·8 |

OTHER Li COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 4601·4 | 21726·5 | $1\pi - 3\varphi =$ 21726·4 |
| 19290 | 5182·6 | $2\delta - 3\pi =$ 5184·9 |
| 26875·3 | 3719·9 | $2\sigma - 2\pi =$ 3720·1 |
| 40475 | 2470·0 | $3\delta - 4\delta =$ 2473·9 |
| | | $3\varphi - 4\varphi =$ 2474·3 |
| 7·436μ | 1344·4 | $4\delta - 5\delta =$ 1342·6 |

*Unclassified.*

| λ | ν |
|---|---|
| 23990·8 | 4167 |

The variations in $\Delta\nu$ are believed to be real. It seems probable that the $\sigma$ and $\pi$ pairs are equal, while the smaller values for the $\delta$ pairs are due to normal close satellites.

Combinations are numerous, and in view of the uncertainties in the wave-lengths, the calculated are in satisfactory agreement with the observed positions. The combinations entered as $3\delta-4\delta$ and $4\delta-5\delta$ were respectively given by Dunz as $4\,\Delta p-N/5^2$ $(=3\varphi-N/5^2)$ and $N/5^2-N/6^2$.

Lines 2-7 of the principal series are from observations by Huppers,* and 8-41 from Bevan. The estimated possible error in Bevan's values is $0{\cdot}3A$, but the error in relative positions is probably much smaller. Other lines are from Paschen, Kayser and Runge, and Saunders.

The principal series is represented fairly well by the formula

$$\pi_1(m)=43486{\cdot}3-N/(m+0{\cdot}951125+0{\cdot}007766/m)^2$$

the residuals being

| $m$ | 1 | 2 | 3 | 4 | 5 | 6 | 10 | 15 |
|---|---|---|---|---|---|---|---|---|
| $O-C$ ($\Delta\nu$) | 0·0 | 0·0 | −1·9 | −2·9 | −3·9 | −4·2 | −2·8 | +1·6 |

| $m$ | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|
| $O-C$ ($\Delta\nu$) | +1·0 | +2·1 | −0·1 | −1·1 | 0·0 |

## Sodium.

Na. At. wt. = 23·00 ; At. No. = 11.

The arc lines of sodium form a system of pairs, of which the well-known strong lines in the yellow are the first of the principal series. Other members of the $\pi$ series lie in the ultra-violet, but $\sigma$ and $\delta$ are almost entirely in the visible spectrum. The fundamental series lies in the red and infra-red.

The principal series has been traced in the absorption spectrum as far as the 57th member by Wood and Fortrat,† who measured the positions of the lines on the international scale with great accuracy ; the wave-lengths tabulated are as given by them, and have been re-reduced to wave-numbers in vacuo with the aid of the Washington tables. The following formulæ have been calculated :—

$$\pi_1(m)=41449{\cdot}00-N/(m+1{\cdot}148066-0{\cdot}031200/m)^2$$

$$\pi_2(m)=41449{\cdot}00-N/(m+1{\cdot}147231-0{\cdot}031108/m)^2$$

For $\pi_1$ the residuals are

| $m$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 10 |
|---|---|---|---|---|---|---|---|---|
| $O-C(\Delta\nu)$ | 0·00 | +1·43 | 0·00 | −0·33 | +0·08 | −0·11 | −0·26 | −0·39 |

| $m$ | 15 | 20 | 30 | 35 | 40 | 45 | 50 |
|---|---|---|---|---|---|---|---|
| $O-C(\Delta\nu)$ | −0·38 | +0·18 | +0·22 | −0·25 | −0·10 | −0·04 | −0·01 |

| $m$ | 54 | 55 | 56 | 57 |
|---|---|---|---|---|
| $O-C(\Delta\nu)$ | −0·01 | −0·24 | −0·81 | −1·34 |

It is clear that the simple formula does not accurately represent the series, although the residuals rarely exceed a few hundredths of an angstrom. Hicks‡ has

* Zeit. f. Wiss. Phot., **13**, 46 (1914).
† Astrophys. Jour., **43**, 73 (1916).
‡ Astrophys. Jour., **44**, 231 (1916).

## Na Doublets.

**Principal. $1\sigma - m\pi$. $1\sigma = 41449{\cdot}00$.**

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 5889·963(8*R*) | 16973·35 | 17·18 | (1) | 24475·65 |
| 95·930(10*R*) | 956·17 | | | 24492·83 |
| 3302·34 (7*R*) | 30272·86 | 5·49 | (2) | 11176·14 |
| 02·94 (8*R*) | 267·37 | | | 11181·63 |
| 2852·828(5*R*) | 35042·66 | 2·49 | (3) | 6406·34 |
| 53·031(6*R*) | 040·17 | | | 6408·83 |
| 2680·335(4*R*) | 37297·70 | 1·50 | (4) | 4151·30 |
| 80·443(5*R*) | 296·20 | | | 4152·80 |
| 2593·828 | 38541·54 | 1·47 | (5) | 2907·46 |
| 93·927 | 540·07 | | | 2908·93 |
| 2543·817 | 39299·20 | 0·89 | (6) | 2149·80 |
| 43·875 | 298·31 | | | 2150·69 |
| 2512·123 | 39794·92 | 1·31 | (7) | 1654·08 |
| 12·210 | 793·61 | | | 1655·31 |
| 2490·733 | 40136·72 | | (8) | 1312·28 |
| 75·533 | 383·14 | | (9) | 1065·86 |
| 64·397 | 565·60 | | (10) | 883·40 |
| 55·915 | 705·69 | | (11) | 743·31 |
| 49·393 | 814·08 | | (12) | 634·92 |
| 44·195 | 900·87 | | (13) | 548·13 |
| 40·046 | 970·41 | | (14) | 478·59 |
| 36·627 | 41027·90 | | (15) | 421·10 |
| 33·824 | 075·14 | | (16) | 373·86 |
| 31·433 | 41115·53 | | (17) | 333·47 |
| 29·428 | 149·46 | | (18) | 299·54 |
| 27·705 | 178·67 | | (19) | 270·33 |
| 26·217 | 41203·91 | | (20) | 245·09 |
| 24·937 | 225·65 | | | 223·35 |
| 23·838 | 244·35 | | | 204·65 |
| 22·856 | 261·07 | | | 187·93 |
| 21·997 | 275·70 | | | 173·30 |
| 21·233 | 288·72 | | (25) | 160·28 |
| 20·520 | 41300·88 | | | 149·12 |
| 19·922 | 11·07 | | | 137·93 |
| 19·380 | 20·34 | | | 128·66 |
| 18·893 | 28·67 | | | 120·33 |
| ·454 | 36·17 | | (30) | 112·83 |
| ·062 | 42·86 | | | 106·14 |
| 17·695 | 49·11 | | | 99·89 |
| ·362 | 54·83 | | | 94·17 |
| ·058 | 60·03 | | | 88·97 |
| 16·779 | 64·81 | | (35) | 84·19 |
| ·518 | 69·27 | | | 79·73 |
| ·271 | 73·50 | | | 75·50 |
| ·046 | 77·35 | | | 71·65 |
| 15·838 | 80·91 | | | 68·09 |
| ·651 | 84·12 | | (40) | 64·88 |
| ·474 | 87·15 | | | 61·85 |
| ·305 | 90·05 | | | 58·95 |
| ·147 | 92·75 | | | 56·25 |
| ·006 | 95·16 | | | 53·84 |

**Principal. $1\sigma - m\pi$ (*continued*). $1\sigma = 41449{\cdot}00$.**

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 2414·872 | 41397·46 | | (45) | 51·54 |
| ·746 | 9·61 | | | 49·39 |
| ·627 | 41401·66 | | | 47·34 |
| ·518 | 3·53 | | | 45·47 |
| ·411 | 5·37 | | | 43·63 |
| ·313 | 7·06 | | (50) | 41·94 |
| ·218 | 8·69 | | | 40·31 |
| ·131 | 41410·19 | | | 38·81 |
| ·050 | 1·57 | | | 37·43 |
| 13·971 | 2·93 | | | 36·07 |
| ·910 | 3·97 | | (55) | 35·03 |
| ·873 | 4·61 | | | 34·39 |
| ·837 | 5·22 | | | 33·78 |

**Sharp. $1\pi - m\sigma$. $1\pi_1 = 24475{\cdot}65$ ; $1\pi_2 = 24492{\cdot}83$.**

| λ, Int. | ν | Δν | m | mσ |
|---|---|---|---|---|
| —5889·963(8*R*) | —16973·35 | 17·18 | (1) | 41449·00 |
| — 95·930(10*R*) | — 956·17 | | | |
| 11404·2 | 8766·34 | 16·79 | (2) | 15709·50 |
| 382·4 | 8783·13 | | | |
| 6160·725(8*r*) | 16227·37 | 17·17 | (3) | 8248·28 |
| 54·214(8*r*) | 244·54 | | | |
| 5153·645(6*n*) | 19398·34 | 17·17 | (4) | 5077·31 |
| 49·090(5*n*) | 415·51 | | | |
| 4751·891(4*n*) | 21038·37 | 17·18 | (5) | 3437·28 |
| 48·016(3*n*) | 055·55 | | | |
| 4545·218(4*n*) | 21995·00 | 17·18 | (6) | 2480·65 |
| 41·671(3*n*) | 22012·18 | | | |
| 4423·31 (4*n*) | 22601·16 | 17·24 | (7) | 1874·49 |
| 19·94 (3) | 618·40 | | | |
| 4344·8 (3) | 23009·6 | 17·5 | (8) | 1466·0 |
| 41·5 (2) | 027·1 | | | |
| 4290·6 (2) | 23300·3 | 16·8 | (9) | 1175·5 |
| 87·5 (2) | 317·1 | | | |
| 4252·4 (2) | 23509·5 | 17·1 | (10) | 966·1 |
| 49·3 | 526·6 | | | |
| 4223·3 | 23671·4 | 16·8 | (11) | 804·4 |
| 20·3 (2) | 688·2 | | | |
| 4201·0 | 23797·1 | 15·3 | (12) | 679·5 |
| 4198·3 (2) | 812·4 | | | |

## Na DOUBLETS—*Continued.*

DIFFUSE. $1\pi - m\delta$.
$1\pi_1 = 24475{\cdot}65$ ; $1\pi_2 = 24492{\cdot}83$.

| λ, Int. | ν | Δν | m | mδ |
|---|---|---|---|---|
| 8194·82 (10R) | 12199·48 | 17·16 | (2) | 12276·18 |
| 83·30 (8R) | 216·64 | | | |
| 5688·222 (10) | 17575·30 | 17·17 | (3) | 6900·35 |
| 82·675 (8) | 592·47 | | | |
| 4982·867 (6r) | 20063·20 | 17·14 | (4) | 4412·47 |
| 78·608 (5r) | 080·34 | | | |
| 4668·597 (4r) | 21413·73 | 17·16 | (5) | 3061·92 |
| 64·858 (3r) | 430·89 | | | |
| 4497·724 (2n) | 22227·11 | 17·14 | (6) | 2248·56 |
| 94·266 (2n) | 244·25 | | | |
| 4393·45 | 22754·77 | 17·19 | (7) | 1720·88 |
| 90·14 | 771·96 | | | |
| 4324·3 | 23118·7 | 16·6 | (8) | 1357·2 |
| 21·2 | 135·3 | | | |
| 4276·5 | 23377·0 | 17·0 | (9) | 1098·7 |
| 73·4 | 394·0 | | | |
| 4241·6 | 23569·3 | 15·6 | (10) | 907·1 |
| 38·8 | 584·9 | | | |
| 4215·6 | 23714·7 | 15·7 | (11) | 761·7 |
| 12·8 | 730·4 | | | |
| 4195·5 | 23828·3 | 16·4 | (12) | 647·7 |
| 92·6 | 844·7 | | | |
| 4180·0 | 23916·6 | 17·2 | (13) | 559·0 |
| 77·0 | 933·8 | | | |
| 4168 | 23985 | | (14) | 491 |

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 12276{\cdot}18$.

| λ | ν | Δν | m | mφ |
|---|---|---|---|---|
| 18459·5 | 5415·81 | | (3) | 6860·37 |
| 12677·6 | 7885·81 | | (4) | 4390·37 |
| | | calc. | (5) | 3041·5 |

* The lines of this series are very faint, and the wave-lengths uncertain; this is often called the Lenard series.
† Also $\delta_2(5)$.

COMBINATION. $1\pi - m\pi$.*

| λ | ν | ν calc. |
|---|---|---|
| 5532·0 | 18071·6 | $1\pi_1 - 3\pi_1 = 18069{\cdot}3$ |
| 27·5 | 086·5 | $1\pi_2 - 3\pi_2 = 18084{\cdot}0$ |
| 4918·2 | 20327·0 | $1\pi_1 - 4\pi_1 = 20324{\cdot}4$ |
| 13·8 | 345·2 | $1\pi_2 - 4\pi_2 = 20340{\cdot}0$ |
| 4632·9 | 21578·7 | $1\pi_1 - 5\pi_1 = 21568{\cdot}2$ |
| 29·2 | 596·0 | $1\pi_1 - 5\pi_2 = 21583{\cdot}9$ |
| 4472·3 | 22353·6 | $1\pi_1 - 6\pi_1 = 22325{\cdot}9$ |
| 4372 | 22866 | $1\pi_1 - 7\pi_1 = 22821{\cdot}6$ |

OTHER Na COMBINATIONS.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 5675·70(3v) | 17614·1 | $1\pi_1 - 3\varphi = 17615{\cdot}3$ |
| 70·18(3v) | 631·2 | $1\pi_2 - 3\varphi = 17631{\cdot}5$ |
| 4975·9 (1v) | 20091·3 | $1\pi_1 - 4\varphi = 20085{\cdot}3$ |
| 72·8 (1v) | 103·8 | $1\pi_2 - 4\varphi = 20102{\cdot}5$ |
| †4665·0 | 21430 | $1\pi_1 - 5\varphi = 21434{\cdot}1$ |
| 60·0 | 453 | $1\pi_2 - 5\varphi = 21451{\cdot}3$ |
| 22056·9 | 4532·5 | $2\sigma - 2\pi_1 = 4533{\cdot}4$ |
| 22084·2 | 4526·9 | $2\sigma - 2\pi_2 = 4527{\cdot}9$ |
| 3·418μ | 2925 | $2\pi_1 - 3\sigma = 2927{\cdot}9$ |
| 5·430μ | 1841 | $3\sigma - 3\pi_1 = 1841{\cdot}9$ |
| 9·048μ | 1104·9 | $2\delta - 2\pi_1 = 1100{\cdot}0$ |
| 9·085μ | 1100·5 | $2\delta - 2\pi_2 = 1094{\cdot}5$ |
| 23361·0 | 4279·5 | $2\pi_2 - 3\delta = 4281{\cdot}3$ |
| 23391·0 | 4273·9 | $2\pi_1 - 3\delta = 4275{\cdot}8$ |
| 50230 | 1990 | $3\pi_1 - 4\delta = 1993{\cdot}9$ |
| 40449 | 2471·6 | $3\varphi - 4\varphi = 2470{\cdot}0$ |
| 7·443μ | 1343·2 | $4\varphi - 5\varphi = 1348{\cdot}9$ |
| 3427·1(1) | 29170·8 | $1\sigma - 2\delta = 29172{\cdot}8$ |

*Unclassified Lines of* Na.

| λ | ν |
|---|---|
| 7418·0 | 13477·0 |
| 7409·7 | 13492·1 |
| 7377·1 | 13551·7 |
| 7369·1 | 13566·4 |
| 3345·0 | 29886·8 |

drawn attention to the sudden increase of the residuals beyond $m=54$, and has suggested that the last three lines may not belong to the $\pi$ series.

The lines of $\sigma$ from $m=3$ to $m=8$, and of $\delta$ from $m=3$ to $m=7$ are as determined by S. Datta* from photographs of the spectrum of the sodium vapour lamp designed by Lord Rayleigh, in which the lines are very sharply defined. $\delta(2)$ are from observations by Meggers, $\sigma(2)$ from Paschen, and the remainder are as obtained by Zickendraht† in the vacuum arc.

The combinations are almost entirely as given by Dunz from the work of Paschen. $\lambda 40449$ is entered by Dunz as $3\varphi - N/5^2$, and $\lambda 7{\cdot}443\mu$ as $N/5^2 - N/6^2$. Exner and Haschek's line at $\lambda 3427{\cdot}1$ has been included as a previously unrecognised combination.

## Potassium.

K. At. wt. $=39{\cdot}10$; At. No. $=19$.

The arc lines of potassium form a doublet system similar to that of sodium. The first and second $\pi$ pairs, in the red and violet respectively, are developed in the Bunsen flame spectrum. Bevan observed to the 24th member of the $\pi$ series in the absorption spectrum, and the lines from $\pi(10)$ are as given by him. The wavelengths of the principal pairs 2—4, of the $\sigma$ pairs 4—10, of the $\delta$ pairs 4—10, and of the combination pair $1\sigma - 2\delta$, are as determined by S. Datta from observations with Lord Rayleigh's vapour lamp, in which the lines were much less diffuse than in air.

The limits calculated from the $\sigma$ pairs by Datta are 21963·06 and 22020·77, from which the limit of $\pi$ becomes 35005·88. With this limit, the lines $\pi_1(1)$ and $\pi_1(2)$ lead to the formula

$$\pi_1(m) = 35005{\cdot}88 - N/(m + 1{\cdot}296281 - 0{\cdot}061661/m)^2$$

giving the following residuals :—

| $m$ | 1 | 2 | 3 | 4 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|---|---|---|
| $O-C(\Delta\nu)$ | 0·00 | 0·00 | −2·80 | +2·34 | −0·76 | −1·2 | +4·0 | 0·0 |

| $m$ | 21 | 22 | 23 | 24 |
|---|---|---|---|---|
| $O-C(\Delta\nu)$ | −0·6 | +0·2 | +0·8 | −0·2 |

The presence of a satellite in $\delta(2)$ is strongly suggested by the combination $1\sigma - 2\delta$, which was clearly resolved and accurately measured by Datta. The less refrangible component of the combination is the stronger, and it would thus appear that the chief line in $\delta_1(2)$ is abnormally placed on the less refrangible side of the satellite. The terms $2\delta'$ and $2\delta$ entered in the table have been derived from the lines $(1\sigma - 2\delta') - (1\sigma - 1\pi_1)$ and $(1\sigma - 2\delta) - (1\sigma - 1\pi_1)$, thus eliminating errors of measurement of $\delta(2)$. The structure of $\delta(2)$ is probably as follows :

| | $\lambda$ calc. | $\nu$ calc. | $\Delta\nu$ | $\lambda$ obsd. |
|---|---|---|---|---|
| 1st chief line | 11771·5 | 8492·80 | | |
| Satellite | 11767·9 | 8495·54 | 2·74 | 11771·73 |
| 2nd chief line | 11688·3 | 8553·25 | 57·71 | 11689·76 |

The combination $1\sigma - 2\delta, \delta'$ further suggests that the fundamental series should consist of pairs with $\Delta\nu = 2{\cdot}74$.

* Proc. Roy. Soc., A. **99**, 69 (1921).
† Ann. d. Phys., **31**, 233 (1910).

## K Doublets.

**Principal. $1\sigma - m\pi$.**
$1\sigma = 35005{\cdot}88$.

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 7664·94 (10*R*) | 13042·82 | 57·71 | (1) | 21963·06 |
| 99·01 (10*R*) | 12985·11 | | | 22020·77 |
| 4044·140 (8*R*) | 24720·18 | 18·69 | (2) | 10285·70 |
| 4047·201 (6*R*) | 701·49 | | | 304·39 |
| 3446·722 (8*R*) | 29004·70 | 8·15 | (3) | 6001·18 |
| 47·701 (6*R*) | 28996·55 | | | 6009·33 |
| 3217·01 (6*R*) | 31075·88 | 4·83 | (4) | 3930·00 |
| 17·50 (4*R*) | 071·05 | | | 3934·83 |
| 3102·03 (4*R*) | 32227·61 | 2·29 | (5) | 2778·27 |
| 02·25 (2*R*) | 225·32 | | | 2780·56 |
| 3034·82 (4*R*) | 32941·3 | | (6) | 2064·6 |
| 2992·21 (2*R*) | 33410·4 | | (7) | 1595·5 |
| 63·24 (1*R*) | 737·1 | | (8) | 1268·8 |
| 42·7 (1*R*) | 972·5 | | (9) | 1033·4 |
| 27·9 | 34144·2 | | (10) | 861·7 |
| 16·5 | 277·7 | | | 728·2 |
| 07·5 | 383·8 | | | 622·1 |
| 00·3 | 469·1 | | | 536·8 |
| 2894·5 | 538·1 | | | 467·8 |
| 89·6 | 596·7 | | (15) | 409·2 |
| 85·8 | 642·4 | | | 363·5 |
| 82·8 | 678·4 | | | 327·5 |
| 80·2 | 709·7 | | | 296·2 |
| 77·8 | 738·6 | | | 267·3 |
| 75·7 | 764·0 | | (20) | 241·9 |
| 74·0 | 784·6 | | | 221·3 |
| 72·4 | 803·9 | | | 202·0 |
| 71·0 | 820·9 | | | 185·0 |
| 69·9 | 834·2 | | (24) | 171·7 |

**Sharp. $1\pi - m\sigma$.**
$1\pi_1 = 21963{\cdot}06$ ; $1\pi_2 = 22020{\cdot}77$.

| λ, Int. | ν | Δν | m | $m\sigma$ |
|---|---|---|---|---|
| —7664·94 | —13042·82 | 57·71 | (1) | 35005·88 |
| — 99·01 | —12985·11 | | | |
| 12523·0 | 7983·16 | 56·94 | (2) | 13980·28 |
| 434·3 | 8040·10 | | | |
| 6938·98 (8) | 14407·37 | 57·71 | (3) | 7555·69 |
| 11·30 (7) | 465·08 | | | |
| 5802·16 (6*R*) | 17230·20 | 57·77 | (4) | 4732·83 |
| 5782·77 (5*R*) | 287·97 | | | |
| 5339·670 (4*R*) | 18722·56 | 57·84 | (5) | 3240·44 |
| 23·228 (4*R*) | 780·40 | | | |

**Sharp. $1\pi - m\sigma$—*continued*.**
$1\pi_1 = 21963{\cdot}06$ ; $1\pi_2 = 22020{\cdot}77$.

| λ, Int. | ν | Δν | m | $m\sigma$ |
|---|---|---|---|---|
| 5099·180 (3*R*) | 19605·54 | 57·74 | (6) | 2357·51 |
| 84·212 (2*R*) | 663·28 | | | |
| 4956·043 (1*R*) | 20171·61 | 57·63 | (7) | 1791·49 |
| 41·964 (1*R*) | 229·24 | | | |
| 4863·61 | 20555·16 | 58·17 | (8) | 1407·7 |
| 49·88 | 613·33 | | | |
| 4800·16 | 20826·82 | 57·76 | (9) | 1136·2 |
| 4786·89 | 884·58 | | | |
| 4754·54 | 21026·70 | 57·27 | (10) | 936·6 |
| 41·62 | 083·97 | | | |

**Diffuse. $1\pi - m\delta$.**
$1\pi_1 = 21963{\cdot}06$ ; $1\pi_2 = 22020{\cdot}77$.

| λ | ν | Δν | m | $m\delta$ |
|---|---|---|---|---|
| *11771·73 | 8492·64 | 59·6 | (2) | 13467·52δ′ |
| 689·76 | 8552·19 | | | 470·26δ |
| †6965·0 (1) | 14353·6 | 60·0 | (3) | 7608·3 |
| † 36·0 (1) | 413·6 | | | |
| 5832·31 (7*R*) | 17141·13 | 57·78 | (4) | 4821·89 |
| 12·71 (6*R*) | 198·91 | | | |
| 5359·521 (5*R*) | 18653·20 | 57·80 | (5) | 3309·81 |
| 42·974 (4*R*) | 711·00 | | | |
| 5112·204 (3*R*) | 19555·61 | 57·77 | (6) | 2407·42 |
| 5097·144 (2*R*) | 613·38 | | | |
| 4965·038 (1*R*) | 20135·23 | 57·85 | (7) | 1827·76 |
| 50·816 (1*R*) | 193·08 | | | |
| 4869·70 | 20529·46 | 57·77 | (8) | 1433·57 |
| 56·03 | 587·23 | | | |
| 4805·19 | 20805·0 | 61·3 | (9) | 1156·3 |
| 4791·08 | 866·3 | | | |
| 4759·31 | 21005·6 | 60·8 | (10) | 955·9 |
| 45·58 | 066·4 | | | |

* The terms 2δ are calculated from the combination $1\sigma - 2\delta, \delta'$ (*see* text).

† Roughly measured from reproduction in the Paper by Meggers. The lines are abnormally faint.

K DOUBLETS—*Continued.*

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 13470{\cdot}3$.

| $\lambda$ | $\nu$ | $\Delta\nu$ | $m$ | $m\varphi$ |
|---|---|---|---|---|
| 15166·3 | 6591·8 | | (3) | 6878·5 |
| 11027·1 | 9066·1 | | (4) | 4404·2 |
| 9600·04 | 10413·8 | | (5) | 3056·5 |
| 8905·44 | 11226·0 | | (6) | 2244·3 |
| 8504·3 | 11755·5 | | (7) | 1714·8 |

K COMBINATIONS.

| $\lambda$ | $\nu$ | $\nu$ calc. |
|---|---|---|
| 4642·172 (2) | 21535·62 | $1\sigma - 2\delta =$ 21535·62 |
| 41·585 (1) | 538·36 | $1\sigma - 2\delta' =$ 538·36 |
| 27065·6 | 3693·7 | $2\sigma - 2\pi_1 =$ 3694·6 |
| 27215·0 | 3673·5 | $2\sigma - 2\pi_2 =$ 3675·9 |
| 6·431μ | 1554·4 | $3\sigma - 3\pi_1 =$ 1554·5 |
| 6·461μ | 1547·3 | $3\sigma - 3\pi_2 =$ 1546·4 |
| 36626·4 | 2729·5 | $2\pi_1 - 3\sigma =$ 2730·0 |
| 36372·7 | 2748·6 | $2\pi_2 - 3\sigma =$ 2748·7 |
| 37354·3 | 2676·5 | $2\pi_1 - 3\delta =$ 2677·4 |
| 37075·6 | 2696·4 | $2\pi_2 - 3\delta =$ 2696·1 |

K COMBINATIONS—*continued.*

| $\lambda$ | $\nu$ | $\nu$ calc. |
|---|---|---|
| 8·510μ | 1174·8 | $3\pi_1 - 4\delta =$ 1179·3 |
| 8·452μ | 1182·9 | $3\pi_2 - 4\delta =$ 1187·4 |
| 31395 | 3184·5 | $2\delta - 2\pi_1 =$ 3184·6 |
| 31596·8 | 3164·0 | $2\delta - 2\pi_2 =$ 3165·9 |
| 6·203μ | 1611·6 | $3\delta - 3\pi_1 =$ 1607·1 |
| 6·236μ | 1603·1 | $3\delta - 3\pi_2 =$ 1599·0 |
| 7·426μ | 1346·3 | $4\varphi - 5\varphi =$ 1347·7 |
| *3650 | 27390 | $1\sigma - 3\delta =$ 27397·6 |
| *3062 | 32649 | $1\sigma - 6\sigma =$ 32648·4 |

*Unclassified Lines of* K.

| $\lambda$ | $\nu$ |
|---|---|
| 40115·5 | 2492·1 |
| *4600 | 21733 |
| *4120 | 24265 |
| *3580 | 27925 |

* Approximate wave-lengths of faint lines observed by Datta.

It should be noted that several of the calculated combinations agree less closely with the observed values than is shown in the works of Paschen and Dunz. In order to secure better agreement, Paschen assumed a higher value for the wave-length of $\pi_2(2)$ than that given by Kayser and Runge, and he explained that unless such correction were made the discordances of the corresponding combinations were greater than the probable errors of his infra-red measurements. Paschen's assumed wave-length has not been confirmed by Datta.

The intensities are as given by Kayser and Runge, except for the pair at 4642.

## RUBIDIUM.

Rb. At. wt. = 85·45 ; At. No. = 37.

The arc lines of rubidium form a pair system resembling those of sodium and potassium, but with wider separation. The wave-lengths of the principal series from $\lambda$ 3228 onwards have been taken from the list of absorption lines given by Bevan. Other wave-lengths are by Meggers, Kayser and Runge, Paschen, and Randall.

The satellites in $\delta$ would appear to be somewhat abnormal. A satellite is clearly indicated in $\delta(3)$, and the smaller separations of other $\delta$ pairs also suggest the presence of satellites in the usual positions. In $\delta(2)$, however, only two lines have been recorded, and these show the same separation as the $\sigma$ pairs. The real absence of a

## Rb Doublets.

| Principal. $1\sigma - m\pi$. $1\sigma = 33689{\cdot}1$. | | | | | Diffuse. $1\pi - m\delta$. $1\pi_1 = 20872{\cdot}6$; $1\pi_2 = 21110{\cdot}2$. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ | λ, Int. | ν | Δν | m | $m\delta', \delta$ |
| | | | | | 15290·3 | 6538·3 | | (2) | 14334·3 |
| 7800·29 (10*R*) | 12816·5 | 237·6 | (1) | 20872·6 | —— | —— | 237·7 | | —— |
| 7947·64 (8*R*) | 578·9 | | | 21110·2 | 14754·0 | 6776·0 | | | |
| 4201·82 (8*R*) | 23792·5 | 77·5 | (2) | 9896·6 | | | | | |
| 15·56 (7*R*) | 715·0 | | | 9974·1 | 7759·61 (1) | 12883·7 | 3·0 | (3) | 7988·9 |
| | | | | | 57·83 (8) | 886·7 | | | 7985·9 |
| 3587·08 (5*R*) | 27869·9 | 35·0 | (3) | 5819·2 | | | 237·6 | | |
| 91·59 | 834·9 | | | 5854·2 | 7619·12 (8) | 13121·3 | | | |
| 3348·72 (3*R*) | 29853·6 | 19·3 | (4) | 3835·5 | | | | | |
| 50·89 (5*R*) | 834·3 | | | 3854·8 | —— | —— | | (4) | 5002·4 |
| | | | | | 6298·50 (10) | 15872·4 | | | 5000·2 |
| 3228·05 | 30969·5 | 10·3 | (5) | 2719·6 | | | | | |
| 29·13 | 959·2 | | | 2729·9 | 6206·48 (8) | 16107·8 | | | |
| 3157·56 | 31660·9 | 5·6 | (6) | 2028·2 | | | | | |
| 58·12 | 655·3 | | | 2033·8 | —— | —— | | (5) | 3409·6 |
| | | | | | 5724·19 (4*r*) | 17464·9 | | | 3407·7 |
| 3112·83 | 32115·8 | | (7) | 1573·3 | | | | | |
| 3082·27 | 434·3 | | (8) | 1254·8 | 5647·96 (3*r*) | 700·6 | | | |
| 60·50 | 664·9 | | (9) | 1024·2 | | | | | |
| 44·21 | 839·8 | | (10) | 849·3 | | | | | |
| 32·08 | 971·1 | | (11) | 718·0 | —— | —— | | (6) | 2468·2 |
| 22·60 | 33074·5 | | (12) | 614·6 | 5431·62 (2*r*) | 18405·6 | | | 2467·0 |
| 15·04 | 157·4 | | (13) | 531·7 | | | | | |
| 08·91 | 225·0 | | (14) | 464·1 | 5362·75 (2*r*) | 642·0 | | | |
| 03·99 | 279·4 | | (15) | 409·7 | | | | | |
| 2999·84 | 325·5 | | (16) | 363·6 | | | | | |
| 96·39 | 363·8 | | (17) | 325·3 | —— | —— | | (7) | 1868·8 |
| 93·40 | 397·1 | | (18) | 292·0 | 5260·3 | 19005·0 | | | 1867·6 |
| 91·00 | 423·9 | | (19) | 265·2 | | | | | |
| 88·82 | 448·3 | | (20) | 240·8 | 5195·7 | 241·4 | | | |
| 86·89 | 469·9 | | (21) | 219·2 | | | | | |
| 85·33 | 487·4 | | (22) | 201·7 | | | | | |
| 83·93 | 503·1 | | (23) | 186·0 | —— | —— | | (8) | 1464·6 |
| 82·56 | 518·5 | | (24) | 170·6 | 5150·8 | 19409·1 | | | 1463·5 |
| 81·39 | 531·6 | | (25) | 157·5 | | | | | |
| 80·40 | 542·8 | | (26) | 146·3 | 5088·8 | 19645·6 | | | |
| 79·50 | 552·9 | | (27) | 136·2 | | | | | |
| 78·69 | 562·0 | | (28) | 127·1 | | | | | |
| 77·98 | 570·0 | | (29) | 119·1 | —— | —— | | (9) | 1182·7 |
| 77·27 | 33578·0 | | (30) | 111·1 | 5075·8 | 19695·9 | | | 1176·7 |
| | | | | | 16·8 | 927·5 | | | |

Rb DOUBLETS—*Continued.*

SHARP. $1\pi - m\sigma$.
$1\pi_1 = 20872{\cdot}6$; $1\pi_2 = 21110{\cdot}2$.

| λ, Int. | ν | Δν | m | mσ |
|---|---|---|---|---|
| —7800·29(10*R*) | —12816·5 | 237·6 | (1) | 33689·1 |
| —7947·64(8*R*) | — 578·9 | | | |
| 13666·7 | 7314·6 | 237·9 | (2) | 13557·9 |
| 237·0 | 7552·5 | | | |
| 7408·37 (10) | 13494·5 | 237·6 | (3) | 7378·1 |
| 7280·22 (10) | 732·1 | | | |
| 6159·84 (5) | 16229·7 | 237·6 | (4) | 4642·9 |
| 6070·95 (2) | 467·3 | | | |
| 5654·00 | 17681·7 | 237·0 | (5) | 3191·2 |
| 5579·2 | 918·7 | | | |
| 5391·0 | 18544·3 | 237·2 | (6) | 2328·5 |
| 22·9 | 781·5 | | | |
| 5233·8 | 19101·3 | | (7) | 1773·8 |
| 5170·8 | 334·0 | | | |
| 5133·3 | 19475·2 | | (8) | 1397·4 |

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 14334{\cdot}3$.

| λ | ν | Δν | m | mφ |
|---|---|---|---|---|
| 13443·7 | 7436·7 | ... | (3) | 6897·6 |
| 10081·9 | 9916·1 | ... | (4) | 4418·2 |
| 8873·6 | 11266·3 | ... | (5) | 3068·0 |
| 8274·6 | 12081·9 | ... | (6) | 2252·4 |

Rb COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 27319·8 | 3659·4 | $2\sigma - 2\pi_1 =$ 3661·3 |
| 27909·8 | 3582·0 | $2\sigma - 2\pi_2 =$ 3583·8 |
| 38511·4 | 2595·9 | $2\pi_2 - 3\sigma =$ 2596·0 |
| 6·436μ | 1553·3 | $3\sigma - 3\pi_1 =$ 1558·9 |
| 6·567μ | 1522·3 | $3\sigma - 3\pi_2 =$ 1523·9 |
| 22533·0 | 4436·7 | $2\delta - 2\pi_1 =$ 4437·7 |
| 22936·7 | 4358·7 | $2\delta - 2\pi_2 =$ 4360·2 |
| 5165·18 | 19355·0 | $1\sigma - 2\delta =$ 19354·8 |
| 52313·4 | 1911·1 | $2\pi_1 - 3\delta =$ 1910·7 |
| 12924·1 | 7735·4 | $2\sigma - 3\pi_1 =$ 7738·7 |
| 12986·6 | 7698·2 | $2\sigma - 3\pi_2 =$ 7703·7 |
| 46190·1 | 2164·4 | $3\delta - 3\pi_1 =$ 2166·7 |
| 4·637μ | 2156·1 | $3\delta - 3\pi_1 =$ 2166·7 |
| 4·696μ | 2129·0 | $3\delta - 3\pi_2 =$ 2131·7 |

*Unclassified Lines of* Rb.

| λ | ν |
|---|---|
| 39866·9 | 2507·7 |
| 7·428μ | 1345·9 |
| 7·269μ? | 1375·3 |

*Note.*—Meggers has found that a line observed by Eder and Valenta at λ7060 is due to barium; also that the line measured as λ8521 by Eder and λ8513 by Lehmann belongs to caesium.

satellite in $\delta(2)$ is further suggested by the fact that only single lines have been recorded in the fundamental series, and also by the combination $1\sigma - 2\delta$, which only appears as a single line.

The general arrangement of the series is as given by Dunz, who adopted the combinations indicated by Paschen and Randall. For the first two of the unclassified lines Dunz suggested the combinations $(3\varphi - N/5^2)$ and $(N/5^2 - N/6^2)$, giving wave-numbers 2506·1 and 1340·5 respectively; in this connection it may be observed that $4\varphi - 5\varphi = 1350{\cdot}2$.

The limit adopted for $\pi$ is the mean of two closely accordant values deduced by Hicks and Johanson, corrected to the international scale. From this and the first two lines the Hicks formula is

$$\pi_1(m) = 33689{\cdot}1 - N/(m + 1{\cdot}365753 - 0{\cdot}073450/m)^2$$

This represents the lines very closely, as will appear from the following residuals:

| $m$ | 1 | 2 | 3 | 4 | 5 | 6 | 10 | 15 | 20 | 25 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $O-C(\Delta\nu)$ | 0·0 | 0·0 | +0·3 | +0·1 | −0·5 | +0·1 | +0·8 | 0·0 | −0·5 | +0·3 | +0·4 |

## CAESIUM.

Cs. At. wt.=132·8; At. No.=55.

The arc spectrum of caesium is generally similar to those of the other alkali metals, the main differences being that the characteristic pairs have a wider separation, and that satellites in the diffuse series are well-marked. Observations have been very numerous, but the wave-length determinations in many cases still leave much to be desired; they could probably be improved by observations of the vacuum arc.

The series are tabulated in accordance with Dunz, but the more recent data for the red lines given by Meggers and by Meissner have been incorporated. Bevan's observations have been adopted for the principal series from the third pair onwards, and the wave-numbers have been re-calculated. The wave-lengths for the fundamental series, and for the two unclassified pairs having the same separation, are from Meissner.*

The limit adopted for the principal series is that given by Bevan, which, with $\pi_1(1)$ and $\pi_1(2)$, gives the formula

$$\pi_1(m)=31404{\cdot}6-N/(m+1{\cdot}449446-0{\cdot}088246/m)^2$$

The residuals are

| $m$ | 1 | 2 | 3 | 4 | 5 | 10 | 15 | 20 | 25 | 30 | 31 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $O-C(\Delta\nu)$ | 0·0 | 0·0 | −0·7 | +0·1 | −0·1 | +1·5 | −0·2 | +0·2 | −0·3 | +1·3 | +1·0 |

Bevan considered the possible errors in his wave-lengths to be about $0{\cdot}2A$, and the residuals are within this limit throughout.

* New measures of lines in the red have since been published by Meissner (Ann. d. Phys. **65**, 378, June 1921)

## Cs Doublets.

| Principal. $1\sigma - m\pi$. $1\sigma = 31404{\cdot}6$. | | | | | Diffuse. $1\pi - m\delta$. $1\pi_1 = 19672{\cdot}3$; $1\pi_2 = 20226{\cdot}3$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ | λ, Int. | ν | Δν | m | $m\delta'$, δ |
| 8521·12 (10*R*) | 11732·3 | 554·0 | (1) | 19672·3 | 36127·0 | 2767·3 | 97·9 | (2) | 16905·0 |
| 8943·46 (10*R*) | 178·3 | | | 20226·3 | 34892·0 | 2865·2 | | | 16807·1 |
| | | | | | | | 554·1 | | |
| 4555·26 (8) | 21946·5 | 181·4 | (2) | 9458·1 | 30100·0 | 3321·4 | | | |
| 93·16 (6) | 765·4 | | | 9639·2 | | | | | |
| 3876·39 (6) | 25789·9 | 80·6 | (3) | 5614·7 | 9208·40 (1) | 10856·7 | 42·8 | (3) | 8815·6 |
| 88·65 (4) | 709·3 | | | 5695·3 | 9172·23 (2) | 899·5 | | | 8772·8 |
| | | | | | | | 554·0 | | |
| 3611·52 (4) | 27681·3 | 45·1 | (4) | 3723·3 | 8761·35 (5) | 11410·7 | | | |
| 17·41 (2) | 636·2 | | | 3768·4 | | | | | |
| 3476·88 | 28753·2 | 26·8 | (5) | 2651·4 | 6983·37 (5) | 14315·8 | 20·9 | (4) | 5356·5 |
| 80·13 | 726·4 | | | 2678·2 | 73·17 (10) | 336·7 | | | 5335·6 |
| | | | | | | | 554·0 | | |
| 3398·14 | 29419·5 | 17·1 | (6) | 1985·1 | 6723·18 (10) | 14869·8 | | | |
| 3400·00 | 402·4 | | | 2002·2 | | | | | |
| 3347·44 | 29865·0 | 11·4 | (7) | 1539·6 | 6217·27 (1) | 16079·8 | 11·4 | (5) | 3592·7 |
| 48·72 | 853·6 | | | 1551·0 | 12·87 (8) | 091·2 | | | 3581·1 |
| | | | | | | | 553·6 | | |
| 3313·16 | 30174·0 | 8·0 | (8) | 1230·6 | 6010·33 (7) | 16633·4 | | | |
| 14·04 | 166·0 | | | 1238·6 | | | | | |
| 3288·56 | 30399·8 | 5·3 | (9) | 1004·8 | 5847·64 | 17096·2 | 8·6 | (6) | 2575·7 |
| 89·13 | 394·5 | | | 1010·1 | 44·7 | 104·8 | | | 2567·5 |
| | | | | | | | 554·9 | | |
| 3270·44 | 30568·1 | | (10) | 836·0 | 5663·8 | 17651·1 | | | |
| 3256·66 | 697·5 | | (11) | 707·1 | | | | | |
| 45·91 | 799·2 | | (12) | 605·4 | | | | | |
| 37·47 | 879·5 | | (13) | 525·1 | —— | —— | | (7) | 1936·1 |
| 30·58 | 945·3 | | (14) | 459·3 | 5635·22 | 17740·6 | | | 1931·7 |
| 25·00 | 998·8 | | (15) | 405·8 | | | | | |
| 20·23 | 31044·7 | | (16) | 359·9 | 5465·9 | 18290·2 | | | |
| 16·34 | 082·3 | | (17) | 322·3 | | | | | |
| 12·91 | 115·5 | | (18) | 289·1 | | | | | |
| 10·07 | 143·0 | | (19) | 261·6 | —— | —— | | (8) | 1508·3 |
| 07·67 | 166·3 | | (20) | 238·3 | 5502·9 | 18167·3 | | | 1505·0 |
| 05·53 | 187·1 | | (21) | 217·5 | | | | | |
| 03·69 | 205·0 | | (22) | 199·6 | 5340·96 | 718·0 | | | |
| 02·02 | 221·3 | | (23) | 183·3 | | | | | |
| 00·60 | 235·2 | | (24) | 169·4 | | | | | |
| 3199·34 | 247·5 | | (25) | 157·1 | —— | —— | | (9) | 1208·6 |
| 98·14 | 259·2 | | (26) | 145·4 | 5414·2 | 18464·8 | | | 1207·5 |
| 97·17 | 268·7 | | (27) | 135·9 | | | | | |
| 96·09 | 279·2 | | (28) | 125·4 | 5256·79 | 19017·7 | | | |
| 95·31 | 286·9 | | (29) | 117·7 | | | | | |
| 94·48 | 295·0 | | (30) | 109·6 | | | | | |
| 93·83 | 31301·4 | | (31) | 103·2 | —— | —— | | (10) | 996·4 |
| | | | | | 5350·8 | 18683·6 | | | 988·7 |
| | | | | | 5198·8 | 19229·9 | | | |
| | | | | | —— | —— | | (11) | 828·5 |
| | | | | | 5303·8 | 18849·2 | | | 823·1 |
| | | | | | 5153·8 | 19397·8 | | | |

Cs DOUBLETS—*Continued.*

SHARP. $1\pi - m\sigma$.
$1\pi_1 = 19672{\cdot}3$; $1\pi_2 = 20226{\cdot}3$.

| λ, Int. | ν | Δν | m | mσ |
|---|---|---|---|---|
| —8521·12<br>—8943·46 | —11732·3<br>—11178·3 | 554·0 | (1) | 31404·6 |
| 14694·8<br>13588·1 | 6803·3<br>7357·4 | 554·1 | (2) | 12868·9 |
| 7944·11 (6)<br>7609·13 (5) | 12584·5<br>13138·5 | 554·0 | (3) | 7087·8 |
| 6586·94 (5)<br>6354·98 (4) | 15177·4<br>731·4 | 554·0 | (4) | 4494·9 |
| 6034·6<br>5839·11 | 16566·5<br>17121·2 | 554·7 | (5) | 3105·5 |
| 5746·15<br>5568·7 | 17398·1<br>952·6 | 554·5 | (6) | 2274·0 |
| 5574·2<br>5407·3 | 17935<br>18488 | 553 | (7) | 1738 |

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 16807{\cdot}1$; $2\delta' = 16905{\cdot}0$.

| λ, Int. | ν | Δν | m | mφ |
|---|---|---|---|---|
| 10124·1<br>025·4 | 9874·8<br>9972·0 | 97·2 | (3) | 6932·6 |
| 8079·24(8*r*)<br>15·90(8*r*) | 12374·0<br>471·8 | 97·8 | (4) | 4433·1 |
| 7280·34(6*r*)<br>28·85(6*r*) | 13731·9<br>829·7 | 97·8 | (5) | 3075·2 |
| 6871·10(4*n*)<br>25·11(4*n*) | 14549·7<br>647·7 | 98·0 | (6) | 2257·4 |
| 6628·78<br>(6586·07) * | 15081·6<br>179·3 | 97·7 | (7) | 1725·5 |
| 6472·9<br>32·0 | 15444·7<br>542·9 | 98·2 | (8) | 1362·3 |
| 6366·2<br>26·8 | 15703·5<br>801·5 | 98·0 | (9) | 1103·6 |
| 6289·2<br>51·1 | 15896·0<br>992·8 | 96·8 | (10) | 911·6 |
| 6232·2 | 16041·3 | | (11) | 765·8 |

*Unclassified Lines of* Cs.

| λ, Int. | ν | Δν |
|---|---|---|
| 8053·35 (2*v*)<br>7990·68 (2*v*) | 12413·8<br>511·1 | 97·3 |
| 7270·70 (4*v*)<br>7219·70 (4*v*) | 13750·1<br>847·2 | 97·1 |
| 7·425μ | 1346·4 | |
| 7·111μ? | 1405·9 | |
| 6·931μ | 1442·4 | |
| 39398·5 | 2537·5 | |
| 5209 (1) | 19192 | |

Cs COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 29318·3 | 3409·9 | $2\sigma - 2\pi_1 = 3410{\cdot}8$ |
| 30962·9 | 3228·8 | $2\sigma - 2\pi_2 = 3229{\cdot}7$ |
| 42202·3 | 2368·9 | $2\pi_1 - 3\sigma = 2370{\cdot}3$ |
| 39180·1 | 2551·6 | $2\pi_2 - 3\sigma = 2551{\cdot}4$ |
| 6·807μ | 1468·6 | $3\sigma - 3\pi_1 = 1473{\cdot}1$ |
| 7·193μ | 1390·2 | $3\sigma - 3\pi_2 = 1392{\cdot}5$ |
| 13605·2 | 7347·8 | $2\delta - 2\pi_1 = 7349{\cdot}0$ |
| 13761·2 | 7264·9 | $2\delta' - 2\pi_2 = 7265{\cdot}8$ |

* Calculated λ; line obscured by σ(4).

# CHAPTER XIII.

## GROUP Ib.—COPPER, SILVER AND GOLD.

These elements, like the alkali metals which form the first branch of Group I., yield spectra containing doublets. The separations of the pairs, however, are greater in proportion to the atomic weights than in the first sub-group. Thus silver, with atomic weight 108, gives a doublet separation of 920, while caesium with atomic weight 133 gives a separation of 554. In these elements the typical series are not at all well developed, and there are many lines which remain unclassified. The chief lines of copper and silver were classified by Kayser and Runge, and by Rydberg, and several combinations have since been noted by Dunz. As in the spectra of the alkali metals, the first principal pair occurs with positive sign in the principal series.

Extensive discussions of the three spectra in relation to the "oun" have been given by Hicks.* With the aid of the theories of linkages and summation series which he has developed, Hicks has sought to associate a large number of lines with those belonging to the typical series. Some of the individual illustrations, as Hicks acknowledges, are doubtless merely numerical coincidences. It is largely by the indiscriminate association of spark with arc lines that his results have been obtained, and this is in direct opposition to our knowledge of the spark spectra of other elements in which series are well developed.

Among the more recent observations of the spark spectra of the three elements are those by Eder,† covering the region $\lambda 2080 - \lambda 1855$.

### COPPER.

Cu. At. wt. = 63·56; At. No. = 29.

Measures of the arc spectrum of copper have been made by Kayser and Runge and others, and more recently, in Kayser's laboratory, by Huppers‡ and by Hasbach,§ who give wave-lengths on the international scale. Wave-lengths on the new scale have also been given by Meggers in the region $\lambda 8683 - \lambda 6415$.

The lines are very numerous, and only a small percentage has been identified as representing the typical series or their combinations. As shown by Rydberg,‖ however, there are many triplets and pairs having approximately constant differences of wave-number, but these have no obvious relation to the separations in the main series.

The principal series of doublets is apparently represented by a characteristic strong pair in the near ultra-violet, showing appropriate Zeeman patterns; but there is no very convincing representation of the second or succeeding pairs. The position of the second pair was calculated by Randall¶ as 2025·73, 2024·42 (Rowland scale), but Kayser and Runge observed only one line, at 2025·08(2*R*). Two lines in this region have since been photographed by Rubies, and Dr. M. Catalán** has suggested

* Phil. Mag., Cu **39**, 457; Ag **38**, 301; Au **38**, 1 (1919).
† Zeit. f. Wiss. Phot., **14**, 135 (1914).
‡ Zeit. f. Wiss. Phot., **13**, 59.
§ *Ibid.* 399 (1914).
‖ Astrophys. Jour., **6**, 239 (1897).
¶ Astrophys. Jour., **34**, 1 (1911).
** An. Soc. Esp. Fis. y Quim., **15**, 432 (1917).

that they may correspond with the principal pair. The wave-lengths are 2025·1, 2024·11, giving wave-numbers 49364·7, 49389·8, and a separation of 25·1. The probable combinations involving the term $2\pi$, however, suggest a separation of 33, and it is doubtful whether the second pair is really represented in the spectrum. In any case, there would seem to be an unusually rapid fall in intensity in the principal series.

The series are here tabulated as in the memoir of Dunz, except that Hasbach's wave-lengths have been substituted and the wave-numbers re-calculated; the calculated $\pi(2)$ lines have also been slightly modified. The meaning of the term "$\varkappa$" is not clear, but it may be noted that its value approximates to $N/(1{\cdot}5)^2$.

By extrapolation from the terms $2\delta$, $2\delta'$, Hicks has calculated the terms $1\delta$ and $1\delta'$ as 28382·9 and 28410·0, and has suggested that the true fundamental series has these wave-numbers for limits. By extrapolation from $3\varphi(=6880)$ he similarly found 12257·1 as the value of a possible term $2\varphi$; terms for higher orders were also calculated, and he was thus able to compute the whole series from $m=2$ to $m=10$. The actual representatives suggested for this series, however, include two spark lines and one "displaced" line, and in four instances only one component is given. It seems probable, therefore, that the terms $1\delta$ have no real existence, and that the first pair of the fundamental series is represented by the tabulated infra-red lines observed by Randall.

The constant difference lines to which attention was directed by Rydberg are too numerous for reproduction here, but it may be noted that they comprise :—

| | | |
|---|---|---|
| 6 triplets | with $\Delta\nu$ | 129·5, 50·6 |
| 6 pairs | ,, ,, | 129·5 |
| 10 pairs | ,, ,, | 50·6 |
| 7 triplets | ,, ,, | 680,212 |
| 5 pairs | ,, ,, | 680 |
| 8 pairs | ,, ,, | 212 |

Some of the lines are used more than once in forming the combinations.

A consideration of these pairs and triplets, using the probably more accurate values of Hasbach, suggests that some of the supposed constant differences are merely approximate numerical coincidences, though a majority may be sufficiently exact to be significant.

Huppers has also attempted to identify constant-difference pairs, and has suggested a considerable number of pairs with separations averaging about 248, 79, 50 and 16. Most of these, however, are far from exact, and as spark lines have also been introduced, the results do not seem entitled to much weight. The whole question is worthy of further investigation.

There are numerous other lines which do not appear either in the regular series or in the constant difference groups.

The spark spectrum of copper shows a multitude of lines, but regular series have not been traced. It may be remarked that the Cu and $Cu^+$ lines are perhaps but imperfectly distinguishable in the existing tables, as enhanced lines occur quite prominently in the arc if observed near the poles.

The spark spectrum in the Schumann region has been observed by Handke,* and the vacuum-arc spectrum by McLennan.†

* Quoted in Lyman's book, and by McLennan.
† Proc. Roy. Soc., A. **98**, 105 (1920).

## Cu Doublets.

**Principal.** $1\sigma - m\pi$. $1\sigma = 62308{\cdot}0$.

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 3247·55(10R) | 30783·6 | 248·4 | (1) | 31524·4 |
| 73·97(10R) | 535·2 | | | 772·8 |
| ‡[2024·33] | [49383·0] | 32·7 | (2) | [12925·0] |
| ‡[2025·67] | [ 350·3] | | | [ 957·7] |

**Sharp.** $1\pi - m\sigma$. $1\pi_1 = 31524{\cdot}4$; $1\pi_2 = 31772{\cdot}8$.

| λ, Int. | ν | Δν | m | mσ |
|---|---|---|---|---|
| —3247·55 | —30783·6 | 248·4 | (1) | 62308·0 |
| — 73·97 | — 535·2 | | | |
| 8092·76 (10) | 12353·3 | 248·5 | (2) | 19171·1 |
| 7933·19 (10) | 601·8 | | | |
| 4530·84 (6r) | 22064·8 | 248·7 | (3) | 9459·5 |
| 4480·38 (6r) | 313·5 | | | |
| 3861·75 (3n) | 25887·7 | 248·4 | (4) | 5636·7 |
| 25·05 (3) | 26136·1 | | | |

**Diffuse.** $1\pi - m\delta$. $1\pi_1 = 31524{\cdot}4$; $1\pi_2 = 31772{\cdot}8$.

| λ, Int. | ν | Δν | m | $m\delta', \delta$ |
|---|---|---|---|---|
| 5220·04 (6) | 19151·6 | 6·9 | (2) | 12372·8 |
| 18·17 (10) | 158·5 | | | 365·9 |
| | | 248·3 | | |
| 5153·23 (8n) | 19399·9 | | | |
| 4063·30 (4n) | 24603·6 | 3·7 | (3) | 6920·8 |
| 62·69 (6n) | 607·3 | | | 17·1 |
| | | 248·5 | | |
| 4022·67 (6n) | 24852·1 | | | |
| —— | —— | | (4) | 4415·5 |
| 3687·5 (3n) | 27111·0 | | | 13·4 |
| 3654·3 (3n) | 27357·3 | | | |

**Fundamental.** $2\delta - m\varphi$. $2\delta = 12365{\cdot}9$; $2\delta' = 12372{\cdot}8$.

| λ | ν | Δν | m | mφ |
|---|---|---|---|---|
| 18229·5 | 5484·1 | | (3) | 6880·0 |
| 194·7 | 94·6 | | | |
| | | | (4) | [4400·0] |
| | | | (5) | [3056·0] |

## Cu Combinations.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 16008·5 | 6245·0 | $2\sigma - 2\pi_1 = 6246{\cdot}1$ |
| 16653·4 | 6003·2 | $2\pi_1 - 3\delta' = 6004{\cdot}2$ |
| 4056·7 (2n) | 24643·7 | $1\pi_1 - 3\varphi = 24644{\cdot}4$ |
| 4015·8 (1n) | 894·6 | $1\pi_2 - 3\varphi = 24892{\cdot}8$ |
| 3652·40 (1n) | 27371·5 | $1\pi_2 - 4\varphi = 27372{\cdot}8$ |
| 3512·12 (4n) | 28464·7 | $1\pi_1 - 5\varphi = 28468{\cdot}4$ |
| 2369·88 (6) | 42183·4 | $x - 3\varphi = 42182{\cdot}6$ |
| 2238·43 (2n) | 44660·3 | $x - 4\varphi = 44662{\cdot}6$ |
| †5782·16 (8) | 17289·8 | $x - 1\pi_2 = 17289{\cdot}8$ |
| †5700·25 (6) | 538·2 | $x - 1\pi_1 = 17538{\cdot}2$ |
| *2768·89 (3) | 36104·9 | $x - 2\pi_2 = 36104{\cdot}9$ |
| 66·39 (8) | 137·6 | $x - 2\pi_1 = 36137{\cdot}6$ |
| 2723·95 (2) | 36700·5 | $x - 2\delta = 36696{\cdot}7$ |

$x = 49062{\cdot}6$.

* Used in calculation of $2\pi_1$, $2\pi_2$.
† Used in calculation of $x$.
‡ Calc. from combinations $x - 2\pi$.

## Silver.

Ag. At. wt. = 107·88; At. No. = 47.

The arc spectrum of silver includes only a moderate number of lines, some of which are of great intensity. Kayser and Runge's list contains several lines which are not given by Exner and Haschek as appearing in the arc. Further measures

## Ag DOUBLETS.

### PRINCIPAL. $1\sigma - m\pi$.
$1\sigma = 61095{\cdot}9$.

| λ, Int. | | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 3280·66 (10*R*) | 30472·9 | 920·6 | (1) | 30623·0 |
| 3382·86 (10*R*) | 29552·3 | | | 31543·6 |
| §[2061·19] | 48500·1 | 202·9 | (2) | 12595·8§ |
| §[2069·85] | 297·2 | | | 12798·7§ |

### SHARP. $1\pi - m\sigma$.
$1\pi_1 = 30623{\cdot}0$ ; $1\pi_2 = 31543{\cdot}6$.

| λ, Int. | ν | Δ | m | $m\sigma$. |
|---|---|---|---|---|
| —3280·66 (10*R*) | —30472·9 | 920·6 | (1) | 61095·9 |
| —3382·86 (10*R*) | —29552·3 | | | |
| 8273·73 | 12083·1 | 920·4 | (2) | 18540·0 |
| 7688·12 | 13003·5 | | | |
| 4668·52 (8*r*) | 21414·1 | 920·4 | (3) | 9209·0 |
| 4476·12 (6*r*) | 22334·5 | | | |
| 3981·72 (6*r*) | 25107·7 | 918·8 | (4) | 5516·2 |
| 3841·15 (2*r*) | 26026·5 | | | |
| 3709·96 (1*r*) | 26946·8 | 921·8 | (5) | 3675·6 |
| *3587·25 | 27868·6 | | | |
| $\sigma_1$ | | | | |
| *3568·31 | 28016·5 | | (6) | 2606·5 |
| *3487·53 | 28665·5 | | (7) | 1957·5 |
| *3435·87 | 29096·4 | | (8) | 1526·6 |

### Ag COMBINATIONS. $1\pi - 2\pi$.

| λ, Int. | ν | calc. |
|---|---|---|
| †5545·64 (4*r*) | 18027·2 | $1\pi_1 - 2\pi_1 = 18027{\cdot}2$ |
| †5276·2 (1*r*) | 18947·8 | $1\pi_2 - 2\pi_1 = 18947{\cdot}8$ |
| †5333·31 (2*r*) | 18744·9 | $1\pi_2 - 2\pi_2 = 18744{\cdot}9$ |

### Ag COMBINATIONS. $1\pi - m\varphi$.

| λ | ν | ν calc. |
|---|---|---|
| 4212·60 | 23731·7 | $1\pi_1 - 3\varphi = 23731{\cdot}2$ |
| 4055·31 | 24652·1 | $1\pi_2 - 3\varphi = 24651{\cdot}8$ |
| 3810·71 | 26234·4 | $1\pi_1 - 4\varphi = 26236{\cdot}8$ |
| 3682·30 | 27149·3 | $1\pi_2 - 4\varphi = 27157{\cdot}4$ |
| 3681·6 | 154·1 | |

### Ag COMBINATIONS. $2\sigma - 2\pi$.

| λ | ν | ν calc. |
|---|---|---|
| 16819·5 | 5943·9 | $2\sigma - 2\pi_1 = 5944{\cdot}2$ |
| 17415·7 | 5740·4 | $2\sigma - 2\pi_2 = 5741{\cdot}3$ |

### DIFFUSE. $1\pi - m\delta$.
$1\pi_1 = 30623{\cdot}0$ ; $1\pi_2 = 31543{\cdot}6$

| λ, Int. | ν | Δν | m | $m\delta'$, δ |
|---|---|---|---|---|
| 5471·51 (6) | 18271·4 | 20·3 | (2) | 12351·6 |
| ‡ 65·45(10*R*) | 291·7 | 920·5 | | 331·3 |
| ‡5209·08(10*R*) | 19191·9 | | | |
| 4212·60 | 23731·7 | 10·6 | (3) | 6891·4 |
| 10·71 (8*R*) | 742·3 | 920·4 | | 6880·7 |
| 4055·31 (6R) | 24652·1 | | | |
| —— | —— | | (4) | 4394·3 |
| 3810·71 (2*n*) | 26234·4 | | | 4388·6 |
| 3682·30 (2*n*) | 27149·3 | | | |
| —— | —— | | (5) | 3040·2 |
| 3623·85 (1*n*) | 27587·1 | | | 3035·9 |
| *3507·35 | 28503·4 | | | |
| —— | —— | | (6) | 2224·6 |
| *3520·35 | 28398·2 | | | |
| *3409·76 | 29319·2 | | | |
| —— | —— | | (7) | 1698·3 |
| *3456·25 | 28924·8 | | | |
| *3349·66 | 29845·2 | | | |
| *3413·66 | 29285·7 | | (8) | 1337·3 |

### FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 12331{\cdot}3$ ; $2\delta' = 12351{\cdot}6$.

| λ | ν | Δν | m | $m\varphi$ |
|---|---|---|---|---|
| 18382·3 | 5438·6 | 22·1 | (3) | 6891·8 |
| 307·9 | 5460·7 | | | |
| 12551·0 | 7965·4 | | (4) | 4386·2? |

*Observations by Catalán.

†Used in calculation of $2\pi_1$ and $2\pi_2$.

‡Fabry & Perot's wave-lengths are 5465·489, 5209·081.

§Calc. from combinations $1\pi - 2\pi$. Catalán's observed λλ are 2061·7, 2070·3.

on the new scale have been made by Kaspar,* and by Frings.† Measures in the ultra-violet beyond λ2983 have also been given by Huppers‡; the suggested series in this region, however, are probably fictitious. The majority of the lines are somewhat nebulous, and high precision in the measurements is scarcely to be expected.

The series are here tabulated in accordance with the memoir by Dunz, chiefly using Kayser and Runge's wave-lengths, but they have been extended towards the violet as indicated by Catalán.§ The adopted limit has been calculated from the sharp series.

The spark spectrum of silver is much more complex than the arc spectrum, but many of the lines are of low intensity. No series have yet been traced. Hicks,‖ however, has made an extensive investigation of the lines in connection with his theory of linkages. New measures of the spark lines have been made by Frings, Wagner,¶ and Eder.**

## GOLD.

Au. At. wt.=197·2; At. No.=79.

Series have not yet been very clearly traced in the spectrum of gold. Two pairs of lines of equal separation and appropriate to a doublet system of this element were noted by Rydberg, together with a possible diffuse pair and satellite. The latter, however, are probably not significant. An additional pair has since been found through Lehmann's observations†† in the extreme red, showing a line which pairs with one in the orange. The discussion of the spectrum by Hicks also suggested further pairs, but spark lines are involved in some of them, and there is probably only one (4811, 4065) which is real.

Measures of the arc spectrum on the international scale have been made in Kayser's laboratory by Quincke,‡‡ whose values have been adopted for the lines mentioned below, except for Lehmann's line 7509. The four most probable pairs are:

| λ, Int. | ν | Δν |
|---|---|---|
| 7509·5 | 13312·8 | |
| 5837·396 (4) | 17126·19 | 3813·4 |
| 6278·179 (4) | 15923·79 | |
| 5064·616 (2*n*) | 19739·34 | 3815·55 |
| 4811·611 (4*n*) | 20777·27 | |
| 4065·080 (6) | 24592·85 | 3815·58 |
| 2427·978 (10*R*) | 41174·02 | |
| 2675·953 (10*R*) | 37358·78 | 3815·22 |

* Zeit. f. Wiss. Phot., **10**, 53 (1912).
† *Ibid.*, **15**, 165 (1915).
‡ Zeit. f. Wiss. Phot., **13**, 51 (1914).
§ An. Soc. Esp. Fis. y Quim., **15**, 222 (1917).
‖ Phil. Trans., A. **217**, 374 (1918).
¶ Zeit. f. Wiss. Phot., **10** (1912).
** Zeit. f. Wiss. Phot., **13**, 20, and **14**, 137.
†† Ann. d. Phys., **39**, 75 (1912).
‡‡ Zeit. f. Wiss. Phot., **14**, 249 (1915).

The very strong pair in the ultra-violet has usually been regarded as the first of the principal series, analogous with those of Ag and Cu, but Hicks argues against this supposition on the ground that the wave-lengths are not in step with 3280, 3382 for Ag and 3247, 3274 for Cu. It may be remarked, however, that the first principal Li pair is similarly out of step with those of Na and K.

The first pair in the list is assigned to the sharp series by Lehmann and Hicks, forming $\sigma_1(2)$ and $\sigma_2(2)$; the line 5837 gives a Zeeman resolution in accordance with this supposition. The second pair, in association with a line $\lambda 5230{\cdot}306(1n)$, or $\nu 19114{\cdot}03$, is described by Hicks as an inverse set of the diffuse type. The third pair is assigned to the sharp series by Hicks, who also places the limit for $\sigma_1$ at 29470. Assuming the fourth pair to be the first principal, the limit of the principal series would thus be 70664.

The spark spectrum of gold comprises a very large number of lines, but typical series have not been identified.

# CHAPTER XIV.

## GROUP IIA.—THE ALKALINE EARTH METALS.

Apart from beryllium, which requires further investigation in the region of short wave-lengths, the arc spectra of these elements include a triplet system and a system of singlets. There are combinations in each system, and also a certain number of inter-combinations, of which $1S-1p_2$ is of considerable importance in adjusting the limits in the two systems so as to yield accurate combinations.

In each of the triplet systems the limit of the principal series lies on the less refrangible side of the limits of the subordinate series, and the first principal line appears with negative sign in the principal series and with positive sign in the sharp series. In the formulæ for the sharp series, Rydberg's $\mu$ has to be given a value $>1$ in order that $m=1$ may give the first line. The diffuse series differ from those of the alkali metals in exhibiting lines corresponding to $m=1$ (except in the case of Mg) when $\mu$ is put $<1$. The numeration of the diffuse series also differs from that adopted in the alkalis, and is possibly not altogether satisfactory. In the alkalis, lines of the diffuse series were assigned the same numbers as the lines of the sharp series to which they were nearest, but to do this in the alkaline earth metals would require either that the first diffuse triplet should be numbered zero, or that the first sharp and principal triplet should be given the order-number 2. That the actual first $d$ triplets have been recorded is indicated by their connection with the $f$ series.

In the singlet systems, the component series are arranged in the same way as in lithium, and the chief difference lies in the appearance of lines corresponding to $m=1$ in the diffuse series, except in the case of magnesium.

The enhanced lines form systems of pairs, having $4N$ for the series constant, and showing no simple relations to the arc series. These are tabulated under the headings "ionised Mg" ($Mg^+$), &c. In each case the arc is a sufficient stimulus to excite some of the enhanced lines quite strongly, but these lines are more especially developed in the spark (*see* Plate IV.).

### MAGNESIUM.

Mg. At. wt.=24·32 ; At. No.=12.

The infra-red lines are from observations by Paschen. Of the remaining lines, most of the wave-lengths are from a paper by Fowler and Reynolds,* but a few are from measures by Lorenser and by Meggers. In the case of the triplets the limits adopted for the subordinate series are as calculated by Fowler and Reynolds, corrected to the international scale.

The less refrangible components of the triplets are represented approximately by the following formulæ :—

$$s_1(m)=39760{\cdot}5-N/(m+1{\cdot}376546-0{\cdot}062064/m)^2$$
$$d_1(m)=39760{\cdot}5-N/(m+0{\cdot}832086-0{\cdot}008310/m)^2$$

* Proc. Roy. Soc., A. **89**, 137 (1913).

## Mg TRIPLETS.

### PRINCIPAL. $1s—mp$. $1s=20474\cdot5$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| —5183·67 (10) | —19286·0 | 40·9 | (1) | 39760·5 |
| — 72·70 (9) | — 326·9 | 19·9 | | 39801·4 |
| — 67·38 (8) | — 346·8 | | | 39821·3 |
| 15023·3 | 6654·5 | 4·1 | (2) | 13820·0 |
| 032·7 | 50·4 | | | 824·1 |
| 032·7 | 50·4 | | | 824·1 |
| 7657·5 | 13055·5 | | (3) | 7419·0 |
| 6318·55 | 15822·6 | | (4) | 4651·9 |
| 6319·08 | 821·3 | | | 4653·2 |
| 5782·10 | 17290·0 | | (5) | 3184·5 |

### SHARP. $1p—ms$. $1p_1=39760\cdot5$; $1p_2=39801\cdot4$; $1p_3=39821\cdot3$.

| λ, Int. | ν | Δν | $m$ | $ms$ |
|---|---|---|---|---|
| 5183·67 (10) | 19286·0 | 40·9 | (1) | 20474·5 |
| 72·70 (9) | 326·9 | 19·9 | | |
| 67·38 (8) | 346·8 | | | |
| 3336·69 (8) | 29961·2 | 40·9 | (2) | 9799·3 |
| 32·14 (7) | 30002·1 | 19·8 | | |
| 29·9[illegible] (6) | 021·9 | | | |
| 2942·10 (6) | 33979·4 | 40·8 | (3) | 5781·3 |
| 38·56 (5) | 34020·2 | 19·6 | | |
| 36·88 (4) | 039·8 | | | |
| * [2781·33 | 35943·6 | 40·7 | (4) | 3817·0 |
| * 78·17 | 984·3 | 19·9 | | |
| * 76·63] | 36004·2 | | | |
| 2698·13 (5) | 37051·7 | 40·6 | (5) | 2709·1 |
| 95·18 (4) | 092·3 | 19·7 | | |
| 93·75 (3) | 112·0 | | | |
| 2649·02 (4) | 37738·6 | 40·6 | (6) | 2022·1 |
| 46·17 (3) | 779·2 | 19·9 | | |
| 44·78 (2) | 799·1 | | | |
| 2617·48 (3) | 38193·3 | 41·3 | (7) | 1567·0 |
| 14·65 (2) | 234·6 | | | |
| 2595·92 (2) | 38510·4 | 40·6 | (8) | 1250·3 |
| 93·19 (1) | 551·0 | | | |

* Calculated lines, the real lines being obscured.

### DIFFUSE. $1p—md$. $1p_1=39760\cdot5$; $1p_2=39801\cdot4$; $1p_3=39821\cdot3$.

| λ, Int. | ν | Δν | $m$ | $md$ |
|---|---|---|---|---|
| 3838·29 (10) | 26045·9 | 40·7 | (2) | 13714·7 |
| 32·31 (10) | 086·6 | 20·1 | | |
| 3229·36 (9) | 106·7 | | | |
| 3096·91 (9) | 32280·9 | 41·1 | (3) | 7479·5 |
| 92·97 (8) | 322·0 | 19·8 | | |
| 91·07 (6) | 341·8 | | | |
| 2851·65 (8) | 35057·1 | 39·6 | (4) | 4704·1 |
| 48·43 (7) | 096·7 | 20·5 | | |
| 46·77 (6) | 117·2 | | | |
| 2736·53 (7) | 36531·8 | 40·0 | (5) | 3229·3 |
| 33·54 (6) | 571·8 | 19·8 | | |
| 32·06 (5) | 591·6 | | | |
| 2672·43 (6) | 37408·1 | 40·2 | (6) | 2352·9 |
| 69·56 (5) | 448·3 | 19·9 | | |
| 68·14 (4) | 468·2 | | | |
| 2632·88 (5) | 37970·0 | 41·0 | (7) | 1790·3 |
| 30·04 (4) | 38011·0 | 20·3 | | |
| 28·63 (4) | 031·3 | | | |
| 2606·64 (4) | 38352·1 | 40·5 | (8) | 1408·5 |
| 03·89 (3) | 392·6 | 20·5 | | |
| 02·50 (2) | 413·1 | | | |
| 2588·28 (3) | 38624·2 | 40·9 | (9) | 1136·4 |
| 85·54 (2) | 665·1 | 19·6 | | |
| 84·23 (2) | 684·7 | | | |
| 2574·93 (3) | 38824·4 | 40·4 | (10) | 936·1 |
| 72·25 (2) | 864·8 | 20·9 | | |
| 70·87 (1) | 885·7 | | | |
| 2564·91 (2) | 38976·0 | 41·1 | (11) | 784·2 |
| 62·21 (1) | 39017·1 | 20·4 | | |
| 60·87 (1) | 037·5 | | | |
| 2557·20 (2) | 39093·5 | 39·6 | (12) | 667·6 |
| 54·61 (1) | 133·1 | | | |
| 2551·13 (2) | 39186·5 | 40·9 | (13) | 574·0 |
| 48·47 (1) | 227·4 | | | |

### COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 15768·3 | 6340·2 | $2p_1—3d=6340\cdot5$ |
| 15759·1 | 6343·9 | $2p_2—3d=6344\cdot6$ |
| 10969·8 | 9113·5 | $2p_1—4d=9115\cdot9$ |
| 10963·2 | 9119·1 | $2p_2—4d=9120\cdot0$ |

## Mg TRIPLETS—*Continued.*

FUNDAMENTAL. $2d—mf$. $2d=13714·7$.

| λ | ν | $m$ | $mf$ |
|---|---|---|---|
| 14877·1 | 6719·9 | (3) | 6994·8 |
| 10812·9 | 9245·7 | (4) | 4469·0 |

COMBINATION. $1p—mf$.

| λ | ν | ν calc. |
|---|---|---|
| 3051 | 32766 | $1p_1—3f=32765·7$ |
| 2833 | 35288 | $1p_1—4f=35291·5$ |
| 2729 | 36633 | $1p_1—5f$ |

COMBINATION. $1p—2p$.

| λ | ν | ν calc. |
|---|---|---|
| 3854·11 | 25939·0 | $1p_1—2p_1=25940·5$ |
| 3848·09 | 979·6 | $1p_2—2p_1=25981·4$ |
| 3844·97 | 26000·6 | $1p_3—2p_1=26001·3$ |
| 3854·53 | 25936·2 | $1p_1—2p_2=25936·4$ |
| 3848·78 | 974·9 | $1p_2—2p_2=25977·3$ |

## Mg SINGLETS.

PRINCIPAL. $1S—mP$.
$1S=61672·1$.

| λ, Int. | ν | $m$ | $mP$ |
|---|---|---|---|
| 2852·11 (10*R*) | 35051·4 | (1) | 26620·7 |
| 2025·82 | 49346·6 | (2) | 12325·5 |
| 1828·1 | 54702 | (3) | 6970 |

SHARP. $1P—mS$.
$1P=26620·7$.

| λ, Int. | ν | $m$ | $mS$ |
|---|---|---|---|
| —2852·11 (10*R*) | —35051·4 | (1) | 61672·1 |
| 11828·8 | 8451·7 | (2) | 18169·0 |
| 5711·09 (4) | 17504·9 | (3) | 9115·8 |
| 4730·16 (2) | 21135·0 | (4) | 5485·7 |
| 4354·36 (1) | 22959·1 | (5) | 3661·6 |

COMBINATION. $2S—mP$.
$2S=18169·0$.

| λ | ν | ν calc. |
|---|---|---|
| —11828·8 | — 8451·7 | $2S—1P=-8451·7$ |
| *17108·1 | 5843·6 | $2S—2P=5843·5$ |
| 8928·97 | 11196·4 | $2S—3P=11199$ |

COMBINATION. $1P—mP$.

| λ | ν | ν calc. |
|---|---|---|
| 4511·2 | 22160·9 | $1P—4P$† $=22162·6$ |
| 4250·8 | 23518·4 | $1P—5P$† $=23528·3$ |
| 4106·6 | 24344·2 | $1P—6P$† $=24351·5$ |
| 4018·1 | 24880·4 | $1P—7P$† $=24885·2$ |

Mg INTER-COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| ‡4571·15 (4) | 21870·7 | $1S—1p_2=21870·7$ |
| 12083·2 | 8273·7 | $2D—3f=8274·1$ |
| 9257·9 | 10798·6 | $2D—4f=10799·9$ |
| 3043·75 | 32844·7 | $1p_3—3P=32850·8$ |
| 2768·47 | 36110·3 | $1p_1—5D=36111·8$ |
| 2765·34 | 36151·2 | $1p_2—5D=36152·7$ |

DIFFUSE. $1P—mD$.
$1P=26620·7$.

| λ, Int. | ν | $m$ | $mD$ |
|---|---|---|---|
| 8806·75 (8) | 11351·8 | (2) | 15268·9 |
| 5528·42 (8*r*) | 18083·3 | (3) | 8537·4 |
| 4703·00 (8*r*) | 21257·1 | (4) | 5363·6 |
| 4351·91 (7*r*) | 22972·0 | (5) | 3648·7 |
| 4167·39 (6*r*) | 23989·1 | (6) | 2631·6 |
| 4057·63 (5*r*) | 24638·0 | (7) | 1982·7 |
| 3986·79 (4*r*) | 25075·8 | (8) | 1544·9 |
| 3938·43 (3*r*) | 25383·7 | (9) | 1237·0 |
| 3904·02 (2*r*) | 25607·4 | (10) | 1012·3 |
| 3878·58 (1) | 25775·3 | (11) | 835·4 |
| 3859·24 (1) | 25904·5 | (12) | 716·2 |

*Unclassified Lines of* Mg.

| λ, Int. | ν |
|---|---|
| 23991·3 (15) | 4167·0 |
| 23977·1 (8) | 4169·5 |
| 23963·6 (5) | 4171·9 |
| 17073·1 | 5855·6 |
| 11054·2? (15) | 9043·9 |
| 7800·4 (1) | 12816·4 |
| 7779·9 (1) | 12850·1 |
| 6332·26 (2) | 15787·8 |
| 6021·70 (1) | 16602·0 |
| 2782·98 (6) | 35922·1 |
| § 81·52 (6) | 941·0 |
| 79·84 (6) | 962·7 |
| § 78·29 (6) | 982·7 |
| § 76·76 (6) | 36002·5 |

* Johanson includes this in the Rydberg series as $—1P+1D$, giving $1D=32464·3$.

† These are terms calculated by Lorenser. The lines were observed by Fowler, and are all faint and diffuse.

‡ Used in calculation of $1S$. This line occurs in the flame spectrum and is strong in the electric furnace at low temperatures.

§ These closely represent a (*s*) triplet, but other lines are probably involved.

The residuals $O-C(\Delta\nu)$ are as follows :—

| $m$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $s$ | 0·0 | 0·0 | −0·5 | −0·8 | −0·8 | −0·6 | −0·8 | −0·5 | | | | | |
| $d$ | | 0·0 | 0·0 | −2·0 | −2·3 | −1·7 | −2·0 | −2·0 | −1·5 | −1·2 | −1·0 | −0·8 | −0·7 |

In the formula for $s$, $\mu$ has been put $>1$ so that $m=1$ gives a positive value, in accordance with the occurrence of the $p$ series on the less refrangible side of $s$. If $\mu$ were $<1$ the formula would suggest a $p$ series in the ultra-violet, but this has not been observed.

Direct calculation of the limit for the diffuse series of singlets gave 26619·2, and thence, by adding the wave-number of the first principal line, 61670·6 for the limit of the principal series. The limits adopted, however, have been derived from the combination $1S-1p_2=21870{\cdot}7$, which gives 61672·1 for $1S$, and thence 26620·7 for $1P$.

The combinations have been taken from the works of Dunz and Lorenser. Attention has already been drawn (p. 37) to the difficulty of representing the singlet $D$ series by a formula.

## Ionised Magnesium ($Mg^+$).

The enhanced lines of magnesium have been the subject of an extended investigation by Fowler.* The spectrum is remarkable for the fact that some of the enhanced lines appear conspicuously in the ordinary arc in air while others associated with them in their series relations only appear in the spark, or in the equivalent conditions in an arc in vacuo (*see also* p. 66). The lines which appear in the arc in air are $\lambda\lambda$ 2936, 2928, 2802, 2795, 2798, 2790, constituting three pairs with a separation in wave-number of 91·5. Two pairs of like separation have been observed in the spark by Lyman at 1753·6, 1750·9, and 1737·8, 1735·0; it is not certain that these appear under ordinary arc conditions.

In the spark in air the majority of the arc lines are present, but the first three pairs above mentioned are strengthened, and there is an intense broad line at $\lambda$4481 (*see* Pl. IV.), together with feeble indications of other extremely nebulous lines, including one about $\lambda$3105. As observed in the arc in vacuo, $\lambda$4481 becomes well-defined, and many other lines appear which are probably so diffuse in the spark as to escape detection. Among the additional lines are a number of doublets having a separation of 30·5, and two series of single lines. Under the conditions of the vacuum arc, the line 4481 is revealed as the leader of a strong series which extends far into the ultra-violet; with high resolution, the first three members have been shown to be very close doublets, having the stronger components on the more refrangible sides, and a constant separation $\Delta\nu$ of 0·99. The other members of the series are too close for resolution with the grating. This series is of the fundamental ($\varphi$) type.

The doublets of separation 91·5, the first of which appears in the arc, as well as in the spark, have been arranged in principal ($\pi$), sharp ($\sigma$), and diffuse ($\delta$) series. Most of the members of the series lie in the Schumann region, outside the range of the observations at present available; their positions, however, can be calculated with considerable certainty from the data given by the parallel series of doublets having separation 30·5. The possible associated fundamental series, given by

* Phil. Trans., A. **214**, 225 (1914).

$1\delta - m\varphi$ (where $1\delta$ is about 110830 and $3\varphi$ about 27467), would lie in the Schumann region, and has not been recorded (*see also* p. 66).

The doublets with separation 30·5* may be regarded as forming a secondary system, based upon the second member of the main principal series, which the calculations prove to have an identical separation. The $\sigma$ and $\delta$ series of this second system are well marked, but the $\pi$ series has only been partially observed. The "4481" series is the fundamental series of this secondary system. The more refrangible (stronger) members of these pairs are closely represented by the formula

$$\varphi(m) = 49777{\cdot}07 - \frac{4 \times 109678{\cdot}3}{\left[m + 0{\cdot}994112 + \frac{0{\cdot}007190}{m}\right]^2}$$

in which the constants have been calculated from the first, second, and eighth lines. The differences $O-C$, in wave-number, for the eight lines are 0·00,† −0·01,† −0·35, −0·32, −0·58, −0·17, −0·11, and 0·00.† Notwithstanding their small magnitude, the residuals are sufficiently systematic to show that the formula is not exact. The largest residual is equivalent to $0{\cdot}03A$. The unresolved lines have been regarded as consisting of two components, separated by 0·99, and since in the resolved lines the more refrangible components have about twice the intensity of the less refrangible, the observed wave-numbers have been increased by 0·33 for comparison with the formula. As in most fundamental series, it will be noted that the value of $\mu$ approximates to unity. The fact that this series consists of doublets indicates the presence of a satellite in the $\delta$ doublet 2798, 2791, with which it is connected. The satellite has not been directly observed, but its presence is indicated by the wider separation of the chief lines as compared with the other doublets of the same system. The arrangement is unusual, as the chief line is displaced to the red side of the presumed satellite, but this accords with the greater intensity of the *more* refrangible components of the 4481 series.

A combination series $3\delta - m\varphi$ is well marked, and the calculated values do not differ greatly from the observed, though the differences are fairly systematic.

The series $3\varphi - m\varphi$ is apparently represented, and is of special interest because the calculated values show a clearly systematic deviation from the observed. The terms involved depend upon observations of great accuracy, and the combinations are independent of the adopted value of the limit of the 4481 series.

The separation 14·1 of the third $\pi$ pair re-appears in the combination $2\delta - 3\pi_{1,2}$.

Formulæ for the individual series were given by Fowler, and served to justify the arrangement of the lines adopted in the accompanying table. All the observed enhanced lines are included in the scheme. In drawing up the table, the limits 49777·0 and 49776·0 have been adopted for the "4481" series, and all the other limits have been derived from these with the aid of observed lines, whether occurring in the main series or in combinations. Thus, starting with $2\delta = 49777{\cdot}0$, we have $1\pi_1 = 2\delta + \delta(2) = 49777{\cdot}0 + 35729{\cdot}44 = 85506{\cdot}44$; and $1\sigma = 1\pi_1 + \pi_1(1) = 85506{\cdot}44 + 35760{\cdot}97 = 121267{\cdot}41$.

* These have sometimes been designated the "FP" (Fowler and Payn) doublets of magnesium.

† Used in calculation of constants.

## $Mg^+$ Doublets.

### Principal. $1\sigma - m\pi$.
$1\sigma = 121267{\cdot}41$.

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 2795·523 (50) | 35760·97 | 91·55 | (1) | 85506·44 |
| 2802·698 (50) | 35669·42 | | | 597·99 |
| 1239·9* | 80651·3 | 30·5 | (2) | 40616·1 |
| 1240·4* | 80620·8 | | | 646·6 |
| 1026·0* | 97469·0 | 14·1 | (3) | 23798·4 |
| 1026·1* | 97454·9 | | | 812·5 |

### Sharp. $1\pi - m\sigma$.
$1\pi_1 = 85506{\cdot}44$ ; $1\pi_2 = 85597{\cdot}99$.

| λ, Int. | ν | Δν | m | $m\sigma$. |
|---|---|---|---|---|
| —2795·523 (50) | —35760·97 | 91·55 | (1) | 121267·4 |
| —2802·698 (50) | —35669·42 | | | |
| 2936·496 (35) | 34044·25 | 91·49 | (2) | 51462·2 |
| 28·625 (35) | 34135·74 | | | |
| 1753·6 | 57027 | 88 : | (3) | 28481·2 |
| 50·9 | 57115 | | | |

### Diffuse. $1\pi - m\delta$.
$1\pi_1 = 85506{\cdot}44$ ; $1\pi_2 = 85597{\cdot}99$.

| λ, Int. | ν | Δν | m | $m\delta$, $\delta'$ |
|---|---|---|---|---|
| 2797·989 (40) | 35729·44 | 0·99 | (2) | 49777·0 |
| † | 35730·43 | 91·46 | | 776·0 |
| 90·768 (40) | 35821·90 | | | |
| 1737·8 | 57546 | 93 : | (3) | 27960 : |
| 35·0 | 57639 | | | |

### Combination, σ Type. $2\pi - m\sigma$.
$2\pi_1 = 40616{\cdot}1$ ; $2\pi_2 = 40646{\cdot}6$.

| λ, Int. | ν | Δν | m | $m\sigma$ |
|---|---|---|---|---|
| * | 12134·9 | 30·5 | (3) | 28481·2 |
| * | 12165·4 | | | |
| 4433·991 (8) | 22546·74 | 30·5 | (4) | 18069·3 |
| 27·995 (7) | 22577·27 | | | |
| 3553·51 (5) | 28133·2 | 30·9 | (5) | 12482·7 |
| 49·61 (4) | 28164·1 | | | |
| 3175·84 (2) | 31478·6 | 30·3 | (6) | 9137·6 |
| 3172·79 (1) | 31508·9 | | | |
| 2971·70 (1) | 33640·9 | 30·4 | (7) | 6975·2 |
| 2969·02 (0) | 33671·3 | | | |
| | | | (8) | 5500·8* |

* Calculated lines or terms.
† Probable satellite.
‡ Not resolved ; 49776·7 adopted for limit.

### Combination, π Type. $2\sigma - m\pi$.
$2\sigma = 51462{\cdot}2$.

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| —2936·496 (35) | —34044·25 | 91·49 | (1) | 85506·45 |
| —2928·625 (35) | —34135·74 | | | 597·94 |
| 9217·4* | 10846·1 | 30·5 | (2) | 40616·1 |
| 43·4* | 10815·6 | | | 646·6 |
| 3613·80 (4) | 27663·82 | 14·07 | (3) | 23798·4 |
| 15·64 (3) | 27649·75 | | | 812·5 |
| 2790·33* | 35827·5 | 7·6 | (4) | 15636·7 |
| 90·92* | 35819·9 | | | 644·3 |

### Combination, δ Type. $2\pi - m\delta$.
$2\pi_1 = 40616{\cdot}1$ ; $2\pi_2 = 40646{\cdot}6$.

| λ, Int. | ν | Δν | m | $m\delta$ |
|---|---|---|---|---|
| * | —9130·4 | 30·5 | (2) | 49777·0 |
| * | —9160·9 | | | |
| 7896·37 | 12660·6 | 30·9 | (3) | 27955·3 |
| 77·13 | 12691·5 | | | |
| 4390·585 (10) | 22769·64 | 30·86 | (4) | 17846·3 |
| 84·643 (8) | 22800·50 | | | |
| 3538·86 (6) | 28249·6 | 30·5 | (5) | 12366·5 |
| 35·04 (5) | 28280·1 | | | |
| 3168·98 (3) | 31546·8 | 30·3 | (6) | 9069·4 |
| 65·94 (2) | 31577·1 | | | |
| 2967·87 (1) | 33684·4 | 30·5 | (7) | 6931·7 |
| 65·19 (0) | 33714·9 | | | |
| | | | (8) | 5471·7* |

### Combination, φ Type. $\left.\begin{matrix}2\delta\\2\delta'\end{matrix}\right\} - m\varphi$
$2\delta' = 49776{\cdot}0$ ; $2\delta = 49777{\cdot}0$.

| λ, Int. | ν | Δν | m | $m\varphi$ |
|---|---|---|---|---|
| 4481·327 } (100) | 22308·58 | 0·99 | (3) | 27467·4 |
| 81·129 } | 22309·57 | | | |
| 3104·805 } (30) | 32198·83 | 0·96 | (4) | 17577·2 |
| 04·713 } | 32199·79 | | | |
| 2660·821 } (10) | 37571·22 | 0·93 | (5) | 12204·8 |
| 60·755 } | 37572·15 | | | |
| ‡2449·573 (6) | 40811·08 | | (6) | 8965·6 |
| ‡2329·58 (5) | 42912·93 | | (7) | 6863·8 |
| ‡2253·87 (4) | 44354·35 | | (8) | 5422·3 |
| ‡2202·68 (3) | 45385·03 | | (9) | 4391·7 |
| 2166·28 (2) | 46147·60 | | (10) | 3629·1 |
| | | | (11) | 3049·0* |

$Mg^+$ DOUBLETS—*Continued.*

| COMBINATION. $3\delta - m\varphi$. $3\delta = 27955{\cdot}3$. | | | |
|---|---|---|---|
| λ, Int. | ν obs. | ν calc. | *m* |
| 6346·67 (5) | 15752·0 | 15750·5 | (5) |
| 5264·14 (5) | 18991·2 | 18989·7 | (6) |
| 4739·59 (5) | 21093·0 | 21091·5 | (7) |
| 4436·48 (5) | 22534·1 | 22533·0 | (8) |
| 4242·47 (4) | 23564·6 | 23563·6 | (9) |
| 4109·54 (3) | 24326·8 | 24326·2 | (10) |
| 4013·80 (2) | 24907·0 | 24906·3 | (11) |

| COMBINATION. $3\varphi - m\varphi$ (?) $3\varphi = 27467{\cdot}4$. | | | |
|---|---|---|---|
| λ, Int. | ν obs. | ν calc. | *m* |
| 6545·80 (5) | 15272·8 | 15262·6 | (5) |
| 5401·05 (5) | 18509·8 | 18501·8 | (6) |
| 4851·10 (5) | 20608·2 | 20603·6 | (7) |
| 4534·26 (4) | 22048·1 | 22045·1 | (8) |
| 4331·93 (3) | 23078·0 | 23075·7 | (9) |
| 4193·44 (2) | 23840·1 | 23838·3 | (10) |
| 4093·90 (1) | 24419·7 | 24418·4 | (11) |

| COMBINATION. $2\delta - 3\pi_{1,2}$. $2\delta = 49776{\cdot}7$. | | | |
|---|---|---|---|
| λ, Int. | ν obs. | ν calc. | Δν |
| 3848·24 (7) | 25964·0 | 25964·2 | 14·6 |
| 3850·40 (6) | 25978·6 | 25978·3 | |

## CALCIUM.

Ca. At. wt.=40·07; At. No.=20.

The arc spectrum of calcium includes a system of triplets and a system of singlets. Lines of a doublet system also occur in the spectrum of the arc, but these belong to ionised calcium ($Ca^+$) and will be considered separately.

Data relating to the arc lines have been collected and much extended by Saunders,* and the series are tabulated as given by him. Many of the adopted measures were made by Crew and McCauley,† who used the vacuum arc, and others were made by A. S. King in the course of his work with the electric furnace. Preliminary observations of the infra-red region were provided by H. M. Randall. A valuable set of wave-lengths has also been given by Holtz.‡

The *p* series of triplets lies in the infra-red, and has only been partially recorded; but the *s*, *d*, and *f* series are well marked in the visible and ultra-violet regions. In the *d* series, the separations of the satellites from the chief lines show marked irregularities, the usual shrinkage continuing only to the fourth member, after which the separations increase; the satellites, however, show constant separations from the third line characteristic of the triplet, and it is therefore the chief components which are abnormally displaced. Reference has already been made to the difficulty of representing the *d* series by formulæ (p. 42). The separations in the *f* triplets show the usual correspondence with those of the satellites of the first *d* triplet. There are indications that the triplets of the *f* series have satellites, as in the case of barium, but the lines are too close for measurement in any but the first.

The *P* series of singlets begins with the well-known flame line 4226A, and all the lines are easily reversed, except the second, which is abnormally faint. This does not reverse, as is also the case with the corresponding lines in Sr and Ba, but

* Astrophys. Jour., **52**, 265 (1920).
† Astrophys. Jour., **39**, 29 (1914).
‡ Zeit. Wiss. Phot., **12**, 201 (1913).

## Ca TRIPLETS.

### PRINCIPAL. $1s—mp$. $1s=17765{\cdot}1$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| — 6162·18(9) | —16223·6 | 105·9 | | 33988·7 |
| — 6122·22(8) | — 329·5 | 52·2 | (1) | 34094·6 |
| — 6102·72(8) | — 381·7 | | | 146·9 |
| 19856·3 | 5034·8 | 19·9 | | *12730·3 |
| 19935·2 | 5014·9 | | (2) | 750·2 |
| | †10987·3 | 7·8 | | 6777·8 |
| | † 979·5 | 4·0 | (3) | 85·6 |
| | † 975·5 | | | 89·6 |
| | †13422·4 | | (4) | 4342·7 |

### SHARP. $1p—ms$. $1p_1=33988{\cdot}7$ ; $1p_2=34094{\cdot}6$ ; $1p_3=34146{\cdot}9$.

| λ, Int. | ν | Δν | $m$ | $ms$ |
|---|---|---|---|---|
| 6162·18 (9) | 16223·6 | 105·9 | | |
| 22·22 (8) | 329·5 | 52·2 | (1) | 17765·1 |
| 02·72 (8) | 381·7 | | | |
| 3973·72 (4) | 25158·4 | 105·9 | | |
| 57·05 (5) | 264·3 | 52·2 | (2) | 8830·3 |
| 48·90 (3) | 316·5 | | | |
| 3487·61 (5) | 28664·9 | 106·0 | | |
| 74·77 (3) | 770·9 | 52·1 | (3) | 5323·8 |
| 68·48 (2) | 823·0 | | | |
| 3286·06 (3) | 30423·1 | 105·8 | | |
| 74·66 (2) | 528·9 | 52·1 | (4) | 3565·6 |
| 69·09 (1) | 581·0 | | | |
| 3180·52 (2) | 31432·5 | 105·8 | | |
| 69·85 (1) | 538·3 | 52·1 | (5) | 2556·2 |
| 64·62 (1) | 590·4 | | | |
| 3117·66 (1) | 32066·3 | 105·9 | | |
| 07·39 (1) | 172·2 | 52·2 | (6) | 1922·4 |
| 02·36 (0) | 224·4 | | | |
| 3076·99 | 32490·1 | 105·7 | | |
| 67·01 | 595·6 | 52·7 | (7) | 1498·6 |
| 62·05 | 648·5 | | | |
| 3049·01 | 32788·2 | 105·8 | | |
| 39·21 | 894·0 | 50·8 | (8) | 1200·3 |
| ‡34·52 | 944·8 | | | |
| 3028·97 | 33005·2 | 104·9 | | |
| 19·37 | 110·1 | — | (9) | 982·5 |
| 3014·01 | 33168·9 | | (10) | 819·8 |

### FUNDAMENTAL. $1d—mf$. $1d=28933{\cdot}5$ ; $1d'=28955{\cdot}2$ ; $1d''=28968{\cdot}8$.

| λ, Int. | ν | Δν | $m$ | $mf$ |
|---|---|---|---|---|
| 4585·92 (2) | 21799·7 | | (3) | 7133·9 |
| 85·87 (6) | 799·5 | 21·5 | | |
| 4581·41 (5) | 21821·2 | 13·6 | | |
| 4578·57 (4) | 21834·8 | | | |
| 4098·55 (4) | 24392·1 | 21·5 | (4) | 4541·5 |
| 94·94 (3) | 413·6 | 13·7 | | |
| 92·65 (2) | 427·3 | | | |
| 3875·81 (4) | 25793·9 | 21·8 | (5) | 3139·5 |
| 72·55 (3) | 815·7 | 13·5 | | |
| 70·51 (2) | 829·2 | | | |
| 3753·37 (1) | 26635·3 | 21·5 | (6) | 2298·1 |
| 50·35 (1) | 656·8 | 14·1 | | |
| 48·37 (1) | 670·9 | | | |
| 3678·24 (2) | 27179·4 | 21·6 | (7) | 1754·1 |
| 75·31 (2) | 201·0 | 13·8 | | |
| 73·45 (1) | 214·8 | | | |
| 3628·60 | 27551·2 | 22·1 | (8) | 1382·3 |
| 25·69 | 573·3 | 12·0 | | |
| § 24·11 | 585·3 | | | |
| 3594·08 | 27815·7 | 21·8 | (9) | 1117·7 |
| 91·26 | 837·5 | 13·8 | | |
| 89·49 | 851·3 | | | |
| 3568·91 | 28009·6 | 24·3 | (10) | 923 |
| 66·12 | 033·9 | 13·9 | | |
| 64·35 | 047·8 | | | |
| 3550·03 | 28158·5 | 23·5 | (11) | 774 |
| 47·38 | 182·0 | 14·3 | | |
| 45·58 | 196·3 | | | |
| 3535·55 | 28273·8 | | (12) | 660 |

* Terms calculated from combination $1d—2p$ are 12729·4, 12749·5, 12756·4.

† Calculated, not observed.

‡ Probably belongs to $d$ series.

§ See also $d$ series.

Ca TRIPLETS—*Continued.*

DIFFUSE. $1p$—$md$.
$1p_1$=33988·7 ; $1p_2$=34094·6 ; $1p_3$=34146·9.

| λ, Int. | ν | Δν | m | md'', d', d | λ, Int. | ν | Δν | m | md'', d', d |
|---|---|---|---|---|---|---|---|---|---|
| 19917·3 | 5019·6 | | (1) | 28969·1 | —— | —— | | (7) | 1848·9 |
| | | 13·3 | | | | | — | | |
| 864·3 | 32·9 | | | 955·2 | 3109·51 | 32150·3 | | | 38·7 |
| | | 22·2 | | | | | 9·6 | | |
| 771·1 | 55·1 | | | 933·5 | 3108·58 | 159·9 | | | 28·8 |
| | | 105·6 | | | | | 105·4 | | |
| 19506·8 | 5125·2 | | | | —— | —— | | | |
| | | 14·3 | | | | | | | |
| 452·6 | 39·5 | | | | 3099·34 | 32255·7 | | | |
| | | 52·1 | | | | | — | | |
| 19310·3 | 5177·3 | | | | 3095·29 | 32298·0 | | | |
| 4456·61(3) | 22432·4 | | (2) | 11556·4 | —— | —— | | (8) | 1551·2 |
| | | 3·7 | | | | | — | | |
| 55·88(5) | 436·1 | | | 552·6 | 3081·55 | 32441·9 | | | 47·0 |
| | | 5·6 | | | | | 7·7 | | |
| 54·77(9) | 441·7 | | | 547·0 | 80·82 | 449·6 | | | 39·1 |
| | | 105·9 | | | | | 105·4 | | |
| 4435·67(8) | 22538·3 | | | | 3071·97 | 32543·2 | | | |
| | | 3·7 | | | | | 4·1 | | |
| 34·95(9) | 542·0 | | | | 71·58 | 547·3 | | | |
| | | 52·1 | | | | | 52·6 | | |
| 4425·43(9) | 22590·4 | | | | 3067·01 | 32595·8 | | | |
| 3644·99(0) | 27427·3 | | (3) | 6561·4 | —— | —— | | (9) | 1272·7 |
| | | 1·7 | | | | | — | | |
| 44·76(3) | 429·0 | | | 59·7 | 3055·55 | 32718·2 | | | 70·7 |
| | | 2·8 | | | | | 2·3 | | |
| 44·40(7) | 431·8 | | | 56·9 | 55·32 | 720·5 | | | 68·2 |
| | | 106·0 | | | | | 105·1 | | |
| 3630·97(2) | 27533·3 | | | | —— | —— | | | |
| | | 1·6 | | | | | — | | |
| 30·75(6) | 534·9 | | | | 3045·75 | 32823·3 | | | |
| | | 52·0 | | | | | — | | |
| 3624·11(6) | 27585·3 | | | | 3041·05 | 32874·0 | | | |
| 3362·28(0) | 29733·3 | | (4) | 4255·5 | —— | —— | | (10) | 1045·4 |
| | | 1·4 | | | | | | | |
| 62·13(2) | 734·7 | | | 54·0 | —— | —— | | | |
| | | 1·8 | | | | | | | |
| 61·92(6) | 736·5 | | | 52·2 | 3034·52 | 32944·8 | | | |
| | | 105·8 | | | | | | | |
| 3350·36(2) | 29839·1 | | | | —— | —— | | | |
| | | 1·5 | | | | | | | |
| 50·20(5) | 840·6 | | | | 3024·93 | 33049·2 | | | |
| | | 52·2 | | | | | | | |
| 3344·51(5) | 29891·3 | | | | 3020·15 | 33101·5 | | | |
| —— | —— | | (5) | 3002·4 | 3018·55 | 33119·1 | | (11) | 869·6 |
| | | — | | | | | | | |
| 3226·13(1) | 30988·1 | | | 00·6 | | | | | |
| | | 2·4 | | | | | | | |
| 25·88(5) | 990·5 | | | 2998·2 | | | | | |
| | | 105·8 | | | 3006·22 | 33254·9 | | (12) | 733·8 |
| 3215·33(1) | 31092·2 | | | | | | | | |
| | | 1·7 | | | | | | | |
| 15·15(3) | 093·9 | | | | | | | | |
| | | 52·3 | | | 2996·67 | 33360·8 | | (13) | 627·9 |
| 3209·93 (3) | 31144·5 | | | | | | | | |
| | | | | | 2988·98 | 33446·7 | | (14) | 541·0 |
| —— | —— | | (6) | 2268·2 | | | | | |
| | | — | | | | | | | |
| 3151·28(1) | 31724·1 | | | 64·5 | | | | | |
| | | 5·3 | | | | | | | |
| 50·75(4) | 729·4 | | | 59·3 | 2982·89 | 33515·2 | | (15) | 473·5 |
| | | 106·0 | | | | | | | |
| 3141·16(0) | 31826·3 | | | | | | | | |
| | | 3·8 | | | | | | | |
| 40·78(2) | 830·1 | | | | | | | | |
| | | 52·4 | | | | | | | |
| 3136·00(2) | 31878·7 | | | | | | | | |

## Ca TRIPLETS—*Continued.*

COMBINATIONS. $1d—mp$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 6169·58(3) | 16204·1 | $1d—2p_1$ = 16204·1 |
| 6161·31(2) | 225·9 | $1d'—2p_1$ = 225·8 |
| 6156·08 | 239·7 | $1d''—2p_1$ = 239·4 |
| 6169·03(2) | 205·6 | $1d'—2p_2$ = 205·7 |
| 6163·75(2) | 219·5 | $1d''—2p_2$ = 219·3 |
| 6166·44(2) | 212·4 | $1d''—2p_3$ = 212·4 |
| 4512·28(1) | 22155·7 | $1d—3p_1$ = 22155·7 |
| 07·85(0) | 177·4 | $1d'—3p_1$ = 177·4 |
| 05·00 | 191·4 | $1d''—3p_1$ = 191·0 |
| 09·45(0) | 169·6 | $1d'—3p_2$ = 169·6 |
| 06·62 | 183·5 | $1d''—3p_2$ = 183·2 |
| 07·42 | 179·5 | $1d''—3p_3$ = 179·2 |
| 4065·44 | 24590·8 | ?$1d—4p_1$ = 24590·8 |
| 4062·49 | 608·7 | ?$1d'—4p_1$ = 24612·5 |

COMBINATION. $2d—mf$.

| λ | ν | ν calc. |
|---|---|---|
| 22655·9 | 4412·9 | $2d—3f$ = 4413·1 |
| 624·6 | 19·0 | $2d'—3f$ = 4418·7 |
| 610·0 | 21·8 | $2d''—3f$ = 4422·5 |
| 14278 | 7002 | $2d—4f$ = 7005·5 |

COMBINATION. $2p—md$.

| λ | |
|---|---|
| 16200·0 | Possibly part of incompletely observed group of six lines of combination $2p—3d$. |
| 162·2 | |
| 144·8 | |

## Ca SINGLETS.

PRINCIPAL. $1S—mP$.* $1S$=49304·8.

| λ, Int. | ν | $m$ | $mP$ |
|---|---|---|---|
| 4226·73(10*R*) | 23652·4 | (1) | 25652·4 |
| †2721·65 | 36731·8 | (2) | 12573·1 |
| 2398·58(2) | 41678·8 | (3) | 7625·9 |
| 2275·49(1) | 43933·3 | (4) | 5371·4 |
| 2200·78(1) | 45425·0 | (5) | 3879·6 |
| 2150·78(1) | 46480·5 | (6) | 2824·6 |
| 2118·68 | 47184·7 | (7) | 2120·3 |
| 2097·49 | 47661·3 | (8) | 1638·2 |
| 2082·73 | 47998·9 | (9) | 1305·9 |
| 2073·04 | 48223·2 | (10) | 1071·6 |
| 2064·77 | 48416·3 | (11) | 888·5 |

SHARP. $1P—mS$. $1P$=25652·4.

| λ, Int. | ν | $m$ | $mS$ |
|---|---|---|---|
| —4226·73(10*R*) | —23652·4 | (1) | 49304·8 |
| 10345·0 | 9664·2 | (2) | 15988·2 |
| 5512·98(4) | 18134·0 | (3) | 7518·4 |
| 4847·29(2) | 20624·4 | (4) | 5028·0 |
| 4496·16 | 22235·1 | (5) | 3417·3 |
| 4312·31 | 23183·0 | (6) | 2469·4 |
| 4203·22 | 23784·7 | (7) | 1867·7 |
| 4132·64 | 24190·9 | (8) | 1461·5 |
| 4084·5 | 24476 | (9) | 1176 |

* Formerly known as SL1 (SL="single line"). A strong series.
† Abnormally faint.
‡ Formerly known as SL3.
§ Formerly known as SL2. Faint and diffuse in air, but of medium strength in vacuum arc.

DIFFUSE. $1P—mD$. $1P$=25652·4.

| λ, Int. | ν | $m$ | $mD$ |
|---|---|---|---|
| | (−1802·9) | (1) | 27455·3 |
| 7326·10(8) | 13646·1 | (2) | 12006·3 |
| 5188·85(3) | 19266·9 | (3) | 6385·5 |
| 4685·26(2) | 21337·7 | (4) | 4314·7 |
| 4412·30 | 22657·7 | (5) | 2994·7 |

FUNDAMENTAL. $1D—mF$.‡ $1D$=27455·3.

| λ, Int. | ν | $m$ | $mF$ |
|---|---|---|---|
| 4878·13(5) | 20494·0 | (3) | 6961·3 |
| 4355·10(5) | 22955·3 | (4) | 4500·0 |
| 4108·55(1) | 24332·7 | (5) | 3122·6 |
| 3972·58(1) | 25165·6 | (6) | 2289·7 |
| 3889·14(1) | 25705·5 | (7) | 1749·8 |
| 3833·96 | 26075·5 | (8) | 1379·8 |
| 3795·62 | 26339·0 | (9) | 1116·3 |
| 3767·42 | 26536·0 | (10) | 919·3 |

COMBINATION. $1D—mP$.§

| λ, Int. | ν | ν calc. |
|---|---|---|
| | (1803) | $1D—1P$ = 1802·9 |
| 6717·69(5) | 14882·0 | $1D—2P$ = 14882·2 |
| 5041·61(3) | 19829·5 | $1D—3P$ = 19829·4 |
| 4526·94(4) | 22083·9 | $1D—4P$ = 22083·9 |
| 4240·46(2) | 23575·8 | $1D—5P$ = 23575·7 |
| 4058·91(0) | 24630·4 | $1D—6P$ = 24630·7 |
| 3946·05(0) | 25334·8 | $1D—7P$ = 25335·0 |
| 3871·54 | 25822·3 | $1D—8P$ = 25817·1 |

Ca SINGLETS—*Continued.*

COMBINATION. $1S—mD$.*

| λ | ν | ν calc. |
|---|---|---|
| 4575·43 | 21849·9 | $1S—1D$=21849·5 |
| 2680·36 | 37297·6 | $1S—2D$ 37298·5 |
| 2329·33 | 42918·0 | $1S—3D$ 42919·3 |
| 2221·91 | 44992·6 | $1S—4D$ 44990·1 |

COMBINATION. $1S—mS$.

| λ | ν | ν calc. |
|---|---|---|
| 2392·22 | 41789·8 | $1S—3S$=41786·4 |
| 2257·40 | 44285·5 | $1S—4S$=44276·8 |
| 2177·8 | 45883 | $1S—5S$=45887·5 |

OTHER COMBINATIONS.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 7645·25(1) | 13076·9 | $1P—2P$=13079·3 |
| 4929·25 | 20281·4 | $1P—4P$=20281·0 |
| | 3412 | $2S—2P$= 3415 |
| | 8359 | $2S—3P$= 8362 |
| | 19935·2 | $1D—3S$=19936·9 |

Ca INTER-COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 6572·78(3) | 15210·3 | $1S—1p_2$=15210·2 |
| 2734·82 | 36554·9 | $1S—2p_2$=36554·6 |
| 3761·70 | 26576·2 | $1p_2—3S$=26576·2 |

Possibly also $1D—2p_1$, $1D—2p_3$, $1D—3p_3$

*Other Unclassified Lines of* Ca.

| λ, Int. | ν | Δν |
|---|---|---|
| 6439·086(9) | 15525·87 | |
| 5857·476(8) | 17067·48 | |
| 5349·470(5) | 18688·25 | |
| 5262·238(3) | 18998·05 | |
| 4307·738(7) | 23207·53 | |
| 4298·989(8) | 23258·17 | |
| 3000·865(4) | 33311·50 | |

*Unclassified Triplets and Pairs of* Ca.

| λ, Int. | ν | Δν |
|---|---|---|
| 4318·648(9) | 23148·91 | 105·85 |
| 4298·989(8) | 254·76 | 52·20 |
| 89·363(9) | 306·96 | |
| 5601·283(5) | 17848·11 | 21·76 |
| 5594·464(8) | 869·87 | 13·92 |
| 90·109(5) | 883·79 | |
| 5270·272(5) | 18969·08 | 21·76 |
| 64·237(3) | 990·84 | 13·93 |
| 60·375(1) | 19004·77 | |
| 7202·161(2) | 13880·89 | 104·94 |
| 7148·123(3) | 985·83 | |
| 4302·525(9) | 23235·66 | 105·87 |
| 4283·008(9) | 341·53 | |
| 3006·864(5) | 33247·58 | 105·99 |
| 2997·309(4) | 353·57 | |
| 6499·648(4) | 15381·20 | 13·88 |
| 93·789(8) | 395·08 | |
| 6471·659(4) | 15447·72 | 21·72 |
| 62·576(9) | 469·44 | |
| 6455·606(3) | 15486·15 | 13·90 |
| 49·811(7) | 500·05 | |
| 5602·829(5) | 17843·18 | 13·85 |
| 5598·484(8) | 857·03 | |
| 5588·746(9) | 17888·15 | 21·70 |
| 81·973(6) | 909·85 | |
| 5265·559(5) | 18986·07 | 13·92 |
| 61·701(3) | 999·99 | |

* Faint and diffuse except in vacuum sources; last two wave-lengths difficult to determine.

the line must belong to the series, because its "term" enters into combinations which appear in the spectrum (see also p. 40). The terms quoted for the $P$ series are averages from $P$ itself and the combination $1D-mP$. Saunders remarks that the courses of the $S$ and $D$ series would have been difficult to trace but for the existence of parallel combination series. In the $D$ series it should be noted that the suggested first line has a negative frequency; it seems necessary to suppose its existence in order to give an appropriate connection with the $F$ lines. Support for the selected $F$ series is given by the close approach of the terms to those of hydrogen (*i.e.*, $\mu$ is nearly unity), which is a general feature of such series.

The limits chosen by Saunders have been adjusted to accord with the interrelations indicated by the various series and combinations, and are believed to have been found with considerable precision.

In addition to combinations in each of the two groups of series, there are lines which result from combinations of terms taken from the singlet and triplet systems. As Saunders remarks, this points to a close relation between the two systems.

There are several interesting triplets and pairs which have not been found to belong to the regular system, although their separations are identical with those observed in the series. These and the brighter unclassified single lines have been included in the tables, as further investigation of possible series or combinations is very desirable.

The intensities shown in the table are those given by Crew and McCauley, as photographed in the vacuum arc. The intensities of the additional lines observed by Saunders have not been stated, but it may be assumed that all the lines for which no intensities are quoted are of low intensity.

## Ionised Calcium ($Ca^+$).

The enhanced lines of calcium form a system of pairs, of which but few occur outside the Schumann region. The well-known $H$ and $K$ lines form the principal pair. Crew and McCauley's wave-lengths have been adopted in the range which they cover, and the remainder are as given by Lyman, except $\delta(1)$, in which case the wave-lengths are the means of the values given by Meggers and Meissner. The separation of the main pairs is 222·85, and that of the narrower fundamental pairs, as indicated by the satellite separation in $\delta$ (1) is 60·85.

The limit 70325·29 was calculated by a Hicks formula from the less refrangible components of the first three $\sigma$ pairs, giving the formula :—

$$\sigma_1(m)=70325{\cdot}29-4N/(m+1{\cdot}205543-0{\cdot}064899/m)^2.$$

The $O-C$ ($\Delta\nu$) equal +0·01,* +0·04,* 0·00,* −18, −24. As shown by Hicks† a more accurate representation of the series is obtained by putting $\mu>1$, and the,re is the additional advantage that $m=1$ then gives the first pair. The first pair of $\delta$ occurs with negative sign, and this also is given by $m=1$, when $\mu$ in that series is taken to be greater than unity. No combination lines have yet been recognised.

* Used in calculation of constants.
† Proc. Roy. Soc., **91**, 452 (1915).

## $Ca^+$ Doublets.

**Principal.** $1\sigma - m\pi$. $1\sigma = 95739{\cdot}70$.

| λ, Int. | ν | Δν | $m$ | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 3933·664(10*R*)<br>3968·465(10*R*) | 25414·41<br>191·56 | 222·85 | (1) | 70325·29<br>548·14 |

**Sharp.** $1\pi - m\sigma$. $1\pi_1 = 70325{\cdot}29$ ; $1\pi_2 = 70548{\cdot}14$.

| λ, Int. | ν | Δν | $m$ | $m\sigma$ |
|---|---|---|---|---|
| —3933·664(10*R*)<br>—3968·465(10*R*) | —25414·41<br>— 191·56 | 222·85 | (1) | 95739·70 |
| 3736·903 (9)<br>06·022 (9) | 26752·55<br>975·46 | 222·91 | (2) | 43572·71 |
| 2208·606 (3)<br>2197·791 (3) | 45263·26<br>485·97 | 222·71 | (3) | 25062·10 |
| 1851·3<br>43·8 | 54016<br>236 | 220 | (4) | 16310 |
| 1698·9<br>92·4 | 58861<br>59087 | 226 | (5) | 11463 |

**Diffuse.** $1\pi - m\delta$. $1\pi_1 = 70325{\cdot}29$ ; $1\pi_2 = 70548{\cdot}14$.

| λ, Int. | ν | Δν | $m$ | $m\delta', \delta$ |
|---|---|---|---|---|
| —8498·00 (8)<br>—8542·15 (10)<br>—8662·11 (9) | —11764·25<br>— 703·44<br>— 541·36 | 60·85<br>222·89 | (1) | 82089·52<br>028·73 |
| 3181·283 (6)<br>79·340(10)<br>58·877(10) | 31424·80<br>443·99<br>647·69 | 19·19<br>222·89 | (2) | 38900·47<br>881·30 |
| ——<br>2112·763 (2)<br>03·239 (2) | ——<br>47316·34<br>530·58 | 8·61<br>222·89 | (3) | 23017·56<br>008·95 |
| 1815·0<br>07·8 | 55096<br>316 | | (4) | 15232 |
| 1680·5<br>74·1 | 59506<br>733 | | (5) | 10815 |

**Fundamental.** $1\delta - m\varphi$. $1\delta = 82029$ ; $1\delta' = 82090$.

| λ | ν | Δν | $m$ | $m\varphi$ |
|---|---|---|---|---|
| 1840·2<br>38·0 | 54341<br>406 | 65 | (3) | 27686 |
| 1555·1<br>53·5 | 64304<br>370 | 66 | (4) | 17723 |
| 1434·3<br>33·1 | 69720<br>778 | 58 | (5) | 12311 |
| 1370·6<br>69·1 | 72960<br>73040 | | (6) | 9060 |

## Strontium.

Sr. At. wt. = 87·63 ; At. No. = 38.

The arc spectrum of strontium is generally similar to that of calcium, consisting of a system of triplets and a system of singlets. The separations of the components of the triplets are greater than those of Ca in approximate proportion to the squares of the atomic weights, and corresponding triplets are displaced to the red with respect to those of Ca.

The chief line of the singlet system is λ 4607, which is the only line of Sr developed in the bunsen flame, and is the leader of the *P* series. As in the case of Ca, the intensities in *P* are somewhat irregular, and the series cannot be represented by a simple formula.

Measurements of the arc and spark lines on the international system have been made by Hampe,* covering the region 7070 to 2428*A*. Observations by Lorenser and

* Zeit. Wiss. Phot., **13**, 348 (1914).

## Sr Triplets.

**Principal.** $1s—mp$.
$1s=16897·8$.

| λ, Int. | ν | Δν | m | $mp_{1,2,3}$ |
|---|---|---|---|---|
| —7070·10(10) | —14140·2 | 394·2 | (1) | 31038·0 |
| —6878·35(10) | — 534·4 | 186·8 | | 432·2 |
| —6791·05(5) | — 721·2 | | | 619·0 |
| 20263 | 4933·8 | | (2) | *11964·0 |
| 9597·0 | 10417·1 | | (3) | †6480·7 |

**Sharp.** $1p—ms$.
$1p_1=31038·0$ ; $1p_2=31432·2$ ; $1p_3=31619·0$.

| λ, Int. | ν | Δν | m | ms |
|---|---|---|---|---|
| 7070·10 )7) | 14140·2 | 394·2 | (1) | 16897·8 |
| 6878·35 (7) | 534·4 | 186·8 | | |
| 6791·05 (6) | 721·2 | | | |
| 4438·04 (4) | 22526·2 | 394·2 | (2) | 8511·8 |
| 4361·71 (4) | 920·4 | 186·8 | | |
| 4326·44 (3) | 23107·2 | | | |
| 3865·46 (4) | 25862·8 | 394·5 | (3) | 5174·9 |
| 07·38 (4) | 26257·3 | 187·0 | | |
| 3780·46 (3) | 444·3 | | | |
| 3628·37 (2) | 27552·7 | 393·2 | (4) | 3485·7 |
| 3577·33 (1) | 945·9 | 187·4 | | |
| 53·5 | 28133·3 | | | |
| 3504·27 (2) | 28528·5 | 394·1 | (5) | 2509·4 |
| 3456·52 (1) | 922·6 | 187·3 | | |
| 34·28 (1) | 29109·9 | | | |

**Fundamental.** $1d—mf$.
$1d=27617·2$ ; $1d'=27717·7$ ; $1d''=27777·6$.

| λ, Int. | ν | Δν | m | $mf'', f', f$ |
|---|---|---|---|---|
| 4893·12 | 20431·2 | 1·8 | (3) | 7186·0 |
| 92·69 (2) | 433·0 | 2·7 | | 84·2 |
| 92·03 (6) | 435·7 | | | 81·5 |
| | | 100·5 | | |
| 4869·19 (3) | 20531·7 | 1·9 | | |
| 68·74 (4) | 533·6 | | | |
| | | 59·7 | | |
| 4855·08 (4) | 20591·4 | | | |
| —— | —— | | (4) | 4571·3 |
| 4337·89 | 23046·2 | 1·0 | | 70·9 |
| 37·70 (4) | 047·2 | | | 70·0 |
| 4319·12 | 23146·4 | 0·5 | | |
| 19·03 (3) | 146·9 | | | |
| | | 59·0 | | |
| 4308·13 (2) | 23205·4 | | | |

**Fundamental.** $1d—mf$ (*continued*).
$1d=27617·2$ ; $1d'=27717·7$ ; $1d''=27777·6$.

| λ | ν | Δν | m | $mf'', f', f$ |
|---|---|---|---|---|
| 4087·46 | 24458·2 | 99·6 | (5) | 3160·5 |
| 70·88 | 557·8 | 59·3 | | 59·9 |
| 61·08 | 617·1 | | | 59·0 |
| 3950·65 | 25305·1 | 100·0 | (6) | 2314·5 |
| 35·10 | 405·1 | 58·0 | | 12·6 |
| 26·14 | 463·1 | | | 12·1 |
| 3867·2 | 25851·2 | | (7) | 1766·0 |

**Diffuse.** $1p—md$.
$1p_1=31038·0$ ; $1p_2=31432·2$ ; $1p_3=31619·0$.

| λ, Int. | ν | Δν | m | $md'', d', d$ |
|---|---|---|---|---|
| —— | (3260·4) | 59·9 | (1) | 27777·6 |
| 30109·7 | 3320·3 | 100·5 | | 717·7 |
| 29225·0 | 3420·8 | | | 617·2 |
| | | 394·2 | | |
| 27355·3 | 3654·6 | 59·9 | | |
| 26914·5 | 3714·5 | | | |
| | | 187·0 | | |
| 26023·6 | 3841·6 | | | |
| 4971·65 (3) | 20108·5 | 15·0 | (2) | 10929·5 |
| 67·93 (4) | 123·5 | 23·1 | | 914·5 |
| 62·24 (6R) | 146·6 | | | 891·4 |
| | | 394·2 | | |
| 4876·06 (6) | 20502·7 | 15·0 | | |
| 72·49 (6) | 517·7 | | | |
| | | 186·6 | | |
| 4832·08 (6) | 20689·3 | | | |
| 4033·19 (0) | 24787·3 | 4·9 | (3) | 6250·7 |
| 32·39 (3) | 792·2 | 12·3 | | 45·8 |
| 30·39 (4) | 804·5 | | | 33·5 |
| | | 394·2 | | |
| 3970·05 (3) | 25181·5 | 4·9 | | |
| 69·27 (3) | 186·4 | | | |
| | | 186·9 | | |
| 3940·8 1 (4) | 25368·4 | | | |

* The terms calculated from combinations $1d—2p$ are 11963·8, 12068·4, 12109·8. These values are further justified by combinations $1D—2p$.

† The probable terms calculated from combinations $1d—3p$ are 6479·1, 6510·2, 6525·0.

## Sr Triplets—*Continued.*

Diffuse. $1p-md$ (*continued*). $1p_1=31038\cdot0$ ; $1p_2=31432\cdot2$ ; $1p_3=31619\cdot0$.

| λ, Int. | ν | Δν | m | md″, d′, d |
|---|---|---|---|---|
| — | — | | (4) | 4072·0 |
| 3706·74 | 26970·2 | 6·1 | | 67·5 |
| 05·90 (3) | 976·3 | | | 61·7 |
| 3653·91 (2) | 27360·2 | 4·8 | | |
| 53·26 (3) | 365·0 | | | |
| | | 186·9 | | |
| 3629·12 (3) | 27547·1 | | | |
| — | — | | (5) | 2869·8 |
| 3548·66 | 28171·7 | 4·5 | | 66·3 |
| 48·09 (4) | 28176·2 | | | 61·8 |
| 3500·11 | 28562·4 | 3·5 | | |
| 3499·68 (4) | 28565·9 | | | |
| | | 186·8 | | |
| 3477·37 (0) | 28749·2 | | | |

| λ | ν | Δν | m | md″, d′, d |
|---|---|---|---|---|
| — | — | | (6) | 2134·7 |
| 3458·47 | 28906·3 | 4·1 | | 31·7 |
| 57·98 | 910·4 | | | 27·6 |
| — | — | | | |
| 3411·94 | 29300·5 | | | |
| 3390·67 | 29484·3 | | | |
| 3401·23 | 29392·8 | | (7) | 1645·2 (*d*) |

Combinations. $1d-mp$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 6386·51 (6) | 15653·6 | $1d-2p_1=$ 15653·6 |
| 45·76 (4) | 754·2 | $1d'-2p_1=$ 754·1 |
| 21·77 (0) | 814·0 | $1d''-2p_1=$ 814·0 |
| 88·25 (6) | 649·3 | $1d'-2p_2=$ 649·3 |
| 63·93 (5) | 709·1 | $1d''-2p_2=$ 709·2 |
| 80·74 (5) | 667·8 | $1d''-2p_3=$ 667·8 |
| 4729·48 (1*n*) | 21138·1 | $1d-3p_1=$ 21138·1 |
| 07·1 (0*n*) | 238·6 | $1d'-3p_1=$ 238·6 |
| 14·0 (0*n*) | 207·5 | $1d'-3p_2=$ 207·5 |
| 04·0 (0*n*) | 252·6 | $1d''-3p_3=$ 252·6 |

## Sr Singlets.

Principal. $1S-mP$.*
$1S=45936\cdot5$.†

| λ, Int. | ν | m | mP |
|---|---|---|---|
| 4607·34 (10*R*) | 21698·4 | (1) | 24238·1 |
| 2931·88 (2) | 34097·8 | (2) | 11838·7 |
| 2569·50 (2) | 38906·4 | (3) | 7030·1 |
| 2428·11 (2) | 41171·8 | (4) | 4764·7 |
| 2354·32 (1) | 42462·1 | (5) | 3474·4 |
| 2307·4 (1) | 43325·5 | (6) | 2611·0 |
| 2275·48 (1) | 43933·3 | (7) | 2003·2 |
| 53·34 (1) | 44364·8 | (8) | 1571·7 |
| 37·4 (1) | 44680·8 | (9) | 1255·7 |
| 25·9 (1) | 44911·5 | (10) | 1025·0 |

Sharp. $1P-mS$.
$1P=24238\cdot1$.

| λ, Int. | ν | m | mS |
|---|---|---|---|
| —4607·34 (10) | —21698·4 | (1) | 45936·5 |
| 11242·3? | 8892·5 | (2) | 15345·6 |
| 5970·10 (3) | 16745·5 | (3) | 7492·6 |
| 5165·46(2) | 19354·0 | (4) | 4884·1 |

Diffuse. $1P-mD$.
$1P=24238\cdot1$.

| λ, Int. | ν | m | mD |
|---|---|---|---|
| | (—1547·9) | (1) | (25786·8) |
| 7621·54 (5) | 13117·1 | (2) | 11121·0 |
| 5543·32 (5) | 18034·7 | (3) | 6203·4 |

Fundamental. $1D-mF$.‡
$1D=25786\cdot8$.

| λ, Int. | ν | m | mF |
|---|---|---|---|
| 5156·07 (4) | 19389·2 | (3) | 6397·6 |
| 4678·30 (4) | 21369·3 | (4) | 4417·5 |
| 4406·11(1) | 22689·4 | (5) | 3097·4 |
| 4252·97 (1) | 23506·4 | (6) | 2280·4 |

* Formerly known as S.L. (single line) No. 1.
† Limit derived from inter-combination $1S-1p_2=\nu14504\cdot3$.
‡ Formerly known as S.L. 3.

## Sr Singlets—*Continued.*

Combination. $1D—mP$.*
$1D=25786·8$.

| λ, Int. | ν | m | ν calc. |
|---|---|---|---|
| 7167·24 (6) | 13948·5 | (2) | 13948·1 |
| 5329·82 (5) | 18757·2 | (3) | 18756·7 |
| 4755·47 (2) | 21022·5 | (4) | 21022·1 |
| 4480·54 (2) | 22312·5 | (5) | 22312·4 |
| 4313·18 (1) | 23178·2 | (6) | 23175·8 |
| 4202·81 (1) | 23787·0 | (7) | 23783·6 |

Combination.

| λ | ν | ν calc. |
|---|---|---|
| 4961·48 | 20149·7 | $1S—1D=20149·7$† |

Sr Inter-combinations.

| λ | ν | ν calc. |
|---|---|---|
| 6892·62 (6) | 14504·3 | $1S—1p_2=14504·3$ |
| 7309·47 (6) | 13677·1 | $1D—2p_3=13677·0$ |
| 7287·44 (1) | 718·5 | $1D—2p_2=13718·4$ |
| 7232·24 (6) | 823·2 | $1D—2p_1=13823·2$ |

*Unclassified Lines of* Sr.

| λ, Int. | ν |
|---|---|
| 20704·8 | 4828·5 |
| 9643·7 | 10366·3 |
| 7673·11 (6) | 13029·0 |
| 7408·08 (3) | 13495·1 |
| 7362·59 (1) | 13578·5 |
| 7348·48 (1) | 13604·5 |
| 7153·08 (4) | 13976·1 |
| 6550·28 (5) | 15262·3 |
| 6465·78 (1) | 15461·8 |
| 6408·49 (9) | 15600·0 |
| 5847·82 (1) | 17095·7 |
| 5816·77 (2) | 17186·9 |
| 5767·05 (2) | 17335·1 |
| 5556·32 (1) | 17992·5 |
| 5521·30 (1) | 18106·7 |
| 5225·11 (5) | 19133·0 |
| 4412·62 (3) | 22655·9 |
| 4140·36 (2) | 24145·7 |
| 4051·0 (1) | 24678·3 |
| 3962·62 (2) | 25228·7 |
| 3371·00 (1) | 29656·3 |
| 3330·01 (4) | 30021·3 |
| 3200·1 | 31240·0 |
| 3199·0 (2) | 31250·8 |
| 3190·1 (2) | 31338·0 |
| 3189·3 (2) | 31345·8 |
| 2549·54 (1) | 39210·9 |
| 2435·55 | 41046·0 |
| 2408·74 | 41502·9 |
| 2138·60? | 46744·7 |
| 2047·28? | 48829·6 |

*Unclassified Triplets and Pairs of* Sr.

| λ, Int. | ν | Δν |
|---|---|---|
| 4876·32 (6) | 20501·6 | 393·9 |
| 4784 39 (4) | 895·5 | 186·8 |
| 4741·99 (5) | 21082·3 | |
| 4811·87 (6*R*) | 20776·2 | 394·1 |
| 4722·27 (6) | 21170·3 | |
| 4531·35 (4) | 22062·3 | 394·2 |
| 4451·80 (3) | 456·5 | |
| 3366·34 (5) | 29697·3 | 394·2 |
| 22·24 (5) | 30091·5 | 186·9 |
| 01·74 (5) | 30278·4 | |
| 3351·26 (6*R*) | 29831·0 | 394·2 |
| 07·55 (4) | 30225·2 | |
| 6446·70 (1) | 15507 5 | 186·8 |
| 6369·96 (6) | 694·3 | |
| 7438·29 (2) | 13440·3 | 58·9 |
| 05·83 (2) | 499·2 | |
| 6643·58 (4) | 15048·0 | 59·8 |
| 17·28 (5) | 107·8 | |
| 6546·82 (4) | 15270·4 | 100·5 |
| 04·02 (6) | 370·9 | |
| 6546·82 (4) | 15270·4 | 59·8 |
| 21·29 (1) | 330·2 | |
| 5693·00 (0) | 17560·6 | 59·4 |
| 73·80 (0) | 620·0 | |
| 5540·11 (5) | 18045·2 | 59·7 |
| 21·83 (6) | 104·9 | |
| 5534·80 (5) | 18062·5 | 100·5 |
| 5504·17 (5) | 163·0 | 59·8 |
| 5486·12 (5) | 222·8 | |
| 5480·84 (7) | 18240·3 | 100·2 |
| 50·91 (6) | 340·5 | |
| 5256·90 (6) | 19017·3 | 100·5 |
| 29·27 (5) | 117·8 | 59·8 |
| 12·97 (2) | 177·6 | |
| 5238·55 (6) | 19084·0 | 59·7 |
| 22·20 (5) | 143·7 | |
| 3182·3 (1) | 31414·7 | 100·0 |
| 72·2 (1) | 514·7 | |

* Formerly known as S.L. 2.
† Used for calculation of $1D$.

by Meggers have also been utilised in drawing up the tables. Other measures, with the vacuum arc as a source, have been communicated to the author by Prof. Saunders, who has also given valuable suggestions as to the allocation of many of the lines.

The $p$ series is at present very imperfectly known, but it has been possible to calculate the probable terms with the aid of certain combinations. The presence of satellites in the $f$ series is very clearly shown.

For the least refrangible components of the sharp series of triplets the formula from the first three lines is

$$s_1(m) = 31037{\cdot}98 - N/(m + 1{\cdot}631561 - 0{\cdot}083879/m)^2,$$

giving residuals $\Delta\nu = -1{\cdot}1$ and $-2{\cdot}9$ for $m = 4$ and 5. The three limits have therefore been adopted as 31038·0, 31432·2 and 31619·0 in accordance with the triplet separations.

The limits for $p$, $d$ and $f$ have been derived in the usual way.*

Limits for the singlet system have been based upon the combination $1S - 1p_2$, except in the case of $F$, for which the limit depends upon the probable combination $1S - 1D$.

As in calcium, there are numerous triplets and pairs which do not fall into the regular systems, and many lines for which places have not been found. These have been tabulated to facilitate further investigations.

Intensities have been inserted when available, and it may generally be assumed that the lines are faint when no intensity numbers appear, except for infra-red lines.

## Ionised Strontium ($Sr^+$).

The enhanced lines of strontium form a pair system analogous with those of calcium and barium. As in the case of those elements, the arc is a sufficient stimulus to develop the lines, but they are relatively more important in the spark, where the ordinary arc lines tend to disappear. (*See* Pl. IV.)

Only one pair of the principal series has been identified. Using the limits calculated for the $\sigma$ pairs, $\pi\infty$ ($=1\sigma$) is found to be $=88{,}952$, and the Rydberg formula indicates a second $\pi$ pair in the region of $\lambda 1810$ with $\Delta\nu$ about 300. No such pair has been noted, and it would seem that the simple Rydberg formula is not sufficiently exact to predict its position.

The sharp series is very closely represented by the formula

$$\sigma_1(m) = 64435{\cdot}80 - 4N/(m + 1{\cdot}304298 - 0{\cdot}083489/m)^2,$$

giving errors 0·0 for the first three lines, and $O - C(\Delta\nu) = +3{\cdot}5$ (or $\Delta\lambda = -0{\cdot}15A$) for

* Note.—Since the above was written, a further communication from Prof. Saunders indicates the observation of many additional lines in extension of several of the series, and new limits are given as follows :—

| | | |
|---|---|---|
| $1p_1 = 31026{\cdot}9$ | $1s = 16887{\cdot}1$ | $1P = 24227{\cdot}1$ |
| $1p_2 = 31421{\cdot}1$ | $1d'' = 27766{\cdot}0$ | $1S = 45925{\cdot}6$ |
| $1p_3 = 31607{\cdot}8$ | $1d' = 27706{\cdot}3$ | $1D = 25776{\cdot}3$ |
| | $1d = 27606{\cdot}0$ | |

As the investigation is not completed, and the combinations and general arrangement of the series are not affected, it has not been thought necessary to adjust the tables to the new limits. Some of the new data, however, have been incorporated.

the fourth. With the same limit, and calculating from $\delta$ (2) and $\delta$ (3), we get the formula

$$\delta_1(m)=64435{\cdot}80-4N/(m+1{\cdot}560163-0{\cdot}106710/m)^2.$$

This represents $\delta_1$ (4) very closely, but extrapolation to $\delta_1$ (1) gives $-8447$ in place of $-9959$. The error, however, is considerably smaller than with the formulæ previously given by Lorenser and Fowler, in which case $\mu$ was put $<1$.* Johanson has applied his formula† to this series, and with the limit 64323·3 adopted from the $\sigma$ series he finds $a=2{\cdot}563879$, $b=-3{\cdot}805663$, $N$ being taken $=4\times109675$. This gives residuals ($\Delta\lambda$) 0·0,‡ 0·0,‡ 0·0,‡ $-1{\cdot}2$, $-1{\cdot}4$.

## $Sr^+$ Doublets.

**Principal. $1\sigma-m\pi$. $1\sigma=88952{\cdot}47$.**

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 4077·71 (10) | 24516·67 | 801·46 | (1) | 64435·80 |
| 4215·52 (9) | 23715·21 | | | 65237·26 |

**Sharp. $1\pi-m\sigma$. $1\pi_1=64435{\cdot}80$; $1\pi_2=65237{\cdot}26$.**

| λ, Int. | ν | Δν | m | $m\sigma$ |
|---|---|---|---|---|
| —4077·71 (10*R*) | —24516·67 | 801·46 | (1) | 88952·47 |
| —4215·52 (9*R*) | —23715·21 | | | |
| 4305·46 (5) | 23219·81 | 801·45 | (2) | 41215·99 |
| 4161·81 (3) | 24021·26 | | | |
| 2471·63 | 40446·92 | 801·64 | (3) | 23988·79 |
| 23·59 | 41248·56 | | | |
| 2051·76 | 48722·98 | 801·98 | (4) | 15712·56 |
| 18·53 | 49524·96 | | | |

**Fundamental. $1\delta-m\varphi$. $1\delta=74115{\cdot}60$; $1\delta'=74395{\cdot}66$.**

| λ, Int. | ν | Δν | m | $m\varphi$ |
|---|---|---|---|---|
| 2165·92 | 46154·84 | 280·76 | (3) | 27960·4 |
| 52·84 | 46435·60 | | | |
| *1778·8 (9) | 56217 | 286 | (4) | 17896 |
| 69·8 (8) | 56503 | | | |
| *1620·7 (5) | 61702 | 283 | (5) | 12412 |
| 13·3 (4) | 61985 | | | |
| *1538 ? (1) | 65020 | | (6) | 9096 |

**Diffuse. $1\pi-m\delta$. $1\pi_1=64435{\cdot}80$; $1\pi_2=65237{\cdot}26$.**

| λ, Int. | ν | Δν | m | $m\delta',\delta$ |
|---|---|---|---|---|
| —10038·0 | —9959·42 | 279·62 | (1) | 74395·66 |
| —10328·0 | —9679·80 | | | 115·60 |
| | | 800·57 | | |
| —10915·4 | —9158·85 | | | |
| 3474·90 (3) | 28769·60 | 85·61 | (2) | 35666·20 |
| 64·47 (7) | 28855·21 | | | 580·59 |
| | | 801·44 | | |
| 3380·72 (6) | 29571·04 | | | |
| 2324·52 | 43006·40 | 39·46 | (3) | 21429·98 |
| 22·39 | 43045·86 | | | 389·94 |
| | | 800·30 | | |
| 2282·05 | 43806·70 | | | |
| — | — | | (4) | 14330·8 |
| 1994·31 | 50126·3 | | | 309·5 |
| 1963·74 | 50906·5 | | | |
| *1847·0 | 54142 | | (5) | 10293 |
| * 20·0 | 54945 | | | |

*Unclassified Lines.*†

| λ | ν |
|---|---|
| *1560·8?(1) | 64070 |
| *1532·3?(1) | 65261 |

* λ vacuum. † Not certainly $Sr^+$.

* Phil. Trans., A. **214**, 237 (1914).
† *See* p. 36.
‡ Used in calculation of constants.

## Barium.

Ba. At. wt. = 137·4 ; At. No. = 56.

A careful study of all the available data for the arc lines of barium has recently been made by Saunders,* who has revised the previously recognised series, and has identified additional combinations. The *f* series is remarkable for the presence of satellites, which are generally similar to those occurring in the *d* series. Both the *f* and *d* series show curious irregularities in the satellite separations ; the data show, however, that the normal triplet separations are maintained by the satellites throughout, and that it is the chief lines which are subject to irregular displacements. There are also irregularities in the intensities of the lines in some of the series. No simple formula of ordinary type will represent the series with reasonable accuracy.

The data chiefly used by Saunders in addition to his own special observations were obtained by King, Randall, Meggers and Eder. Observations of the arc and spark spectra, and comparisons with previous records, have also been given by Schmitz† for the region λ 7,060 to 2,214, and by George‡ for the region λ 7,060 to 8,210.

The tables which follow are a re-arrangement of those given by Saunders, but in some cases the lines have been differently numbered. Thus, in the *f* series, since $\mu$ usually approaches unity in these series, the first triplet has been called (3) in place of the (1) assigned by Saunders.

The intensities in the barium spectrum have been very incompletely recorded ; Kayser and Runge's estimates have been adopted so far as possible. Many lines remain unclassified.

### Ionised Barium ($Ba^+$).

The enhanced lines of barium form a pair system, with satellites, similar to those of Mg, Ca, and Sr. The leading members of the series were recognised by Ritz, and additional members were subsequently traced by Saunders. The series are here given according to Lorenser, except that the new wave-lengths determined by Schmitz have been utilised as far as possible. Lines in the Schumann region are from observations by Lyman.

Hicks§ has adopted the same sets of lines, except for the first member of the $\delta$ series, for which he has selected, as an inverted $\delta$ set,

| λ (Rowland) | ν | Δν |
|---|---|---|
| —5853·91 (10*R*) | —17077·96 | |
| —6148·6 (*ft*) | —16190·53 | 1690·59 |
| —6497·07 (6*R*) | —15387·37 | |

The first line, however, is unduly strong, and the suggested satellite is not only misplaced, but has a separation out of the usual proportion. The infra-red lines assigned by Lorenser are doubtless correct, as they show a satellite separation in agreement with $\Delta\nu$ of the related fundamental series.

* Astrophys. Jour., **51**, 23 (1920).
† Zeit. Wiss. Phot., **11**, 209 (1912).
‡ *Ibid.*, **12**, 257 (1913).
§ Proc. Roy. Soc., A. **91**, 455 (1915).

## Ba TRIPLETS.

### PRINCIPAL. $1s—mp$. $1s=15869\cdot3$.

| λ, Int. | ν | Δν | m | $mp_{1,2,3}$ |
|---|---|---|---|---|
| —7905·80(7) | —12645·5 | 878·2 | (1) | 28514·8 |
| —7392·44(7) | —13523·7 | 370·6 | | 29392·8 |
| —7195·26(6) | —13894·3 | | | 763·3 |
| 20712·0 | 4827·0 | 171·9 | (2) | 11042·3 |
| 21477·2 | 4655·1 | 72·2 | | 214·2 |
| | *4582·9 | | | 286·4 |
| †10189·1 | 9812·1 | 80·1 | (3) | 6057·2 |
| 10272·9 | 9732·0 | 49·6 | | 137·3 |
| 10326· | 9682·4 | | | 186·9 |

### SHARP. $1p—ms$. $1p_1=28514\cdot8$; $1p_2=29392\cdot8$; $1p_3=29763\cdot3$.

| λ | ν | Δν | m | ms |
|---|---|---|---|---|
| 7905·80(7) | 12645·5 | 878·2 | (1) | 15869·3 |
| 7392·44(7) | 13523·7 | 370·6 | | |
| 7195·26(6) | 13894·3 | | | |
| 4902·90(6r) | 20390·5 | 878·2 | (2) | 8124·3 |
| 4700·45(6r) | 21268·7 | 370·5 | | |
| 4619·98(4r) | 21639·2 | | | |
| 4239·56(2r) | 23580·9 | 878·4 | (3) | 4934·0 |
| 4087·31(1n) | 24459·3 | 370·4 | | |
| 4026·30 | 24829·7 | | | |
| 3975·32(2r) | 25148·3 | 878·3 | (4) | 3366·5 |
| 3841·15 | 26026·6 | 370·5 | | |
| 3787·23 | 26397·1 | | | |
| †3828·93 | 26110·3 | 878·2 | (5) | 2404·5 |
| 3704·23 | 26988·5 | | | |

### COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 4674·97 | 21390·5 | $1d—2p_1=$ 21390·7 |
| 4593·16 | 21771·5 | $1d'—2p_1=$ 21771·8 |
| | [obscured] | $1d''—2p_1=$[21953·3] |
| 4629·63 | 21600·0 | $1d'—2p_2=$ 21599·9 |
| 4591·07 | 21781·4 | $1d''—2p_2=$ 21781·4 |
| 4606·38 | 21709·0 | $1d''—2p_3=$ 21709·2 |
| 3790·27 | 26376·9 | $1d—3p_1=$ 26375·8 |
| 26227·44 | 3812·8 | $2d—3f=$ 3813·0 |

* Calculated wave-number.
† Provisionally placed.
‡ Masked by a line of iron impurity.

### DIFFUSE. $1p—md$. $1p_1=28514\cdot8$; $1p_2=29392\cdot8$; $1p_3=29763\cdot3$.

| λ, Int. | ν | Δν | m | $md''$, $d'$, $d$ |
|---|---|---|---|---|
| —22313·4 | —4480·6 | 181·6 | (1) | 32995·6 |
| —23255·3 | —4299·0 | 380·8 | | 814·1 |
| —25515·7 | —3918·2 | | | 433·0 |
| | | 878·0 | | |
| —27751·1 | —3602·6 | 181·5 | | |
| —29233·9 | —3421·1 | | | |
| | | 370·7 | | |
| —30933·8 | —3231·9 | | | |
| 5818·91(4n) | 17180·7 | 55·1 | (2) | 11333·9 |
| 5800·30(6R) | 235·8 | 67·4 | | 279·0 |
| 5777·70(10R) | 303·2 | | | 211·6 |
| | | 878·2 | | |
| 5535·93 | 18058·9 | 55·0 | | |
| 5519·12(8R) | 113·9 | | | |
| | | 370·7 | | |
| 5425·55(8R) | 18429·6 | | | |
| —— | —— | —— | (3) | 6320·1 |
| 4493·66(4v) | 22247·6 | 23·0 | | 267·3 |
| 4489·00(4v) | 270·6 | | | 244·2 |
| 4332·96(4n) | 23072·6 | 52·8 | | |
| 4323·63(4v) | 125·4 | | | |
| | | 370·7 | | |
| 4264·43(4n) | 23443·3 | | | |
| —— | —— | —— | (4) | 4067·5 |
| 4087·31(1n) | 24459·3 | 14·5 | | 55·4 |
| 4084·87(1n) | 473·8 | | | 41·0 |
| 3947·51 | 25325·4 | 12 2 | | |
| 3945·61 | 337·6 | | | |
| | | 370·6 | | |
| 3890·57 | 25696·0 | | | |
| —— | —— | —— | (5) | 2888·7 |
| 3898·58 | 25643·3 | 27·7 | | 71·4 |
| 3894·34 | 671·0 | | | 43·8 |
| 3771·93 | 26504·1 | 17·4 | | |
| 3769·48 | 521·5 | | | |
| | | 370·6 | | |
| 3719·92 | 26874·7 | | | |
| —— | —— | —— | (6) | 2137·1 |
| 3789·72 | 26379·9 | 10·7 | | 34·8 |
| 3788·18 | 390·6 | | | 24·2 |
| 3667·93 | 27255·7 | 2·4 | | |
| 3667·60 | 258·1 | | | |
| ‡(3618·72) | | | | |
| —— | —— | —— | (7) | —— |
| 3721·17 | 26865·7 | 2·3 | | 1649·1 |
| 3720·85 | 868·0 | | | 1646·8 |
| —— | —— | | | |
| 3603·40 | 27743·7 | | | |

## Ba Triplets—*Continued.*

Fundamental. $1d - mf$. $1d = 32433{\cdot}0$ ; $1d' = 32814{\cdot}1$ ; $1d'' = 32995{\cdot}6$.

| λ, Int. | ν | Δν | m | $mf''$, $f'$, $f$ | λ, Int. | ν | Δν | m | $mf''$, $f'$, $f$ |
|---|---|---|---|---|---|---|---|---|---|
| 3997·92 | 25006·1 | | (3) | 7426·8 | — | — | | (8) | 1415·4 |
| 95·66(6) | 020·2 | 14·1 | | 7412·8 | †3222·28 | 31025·1 | | | 07·8 |
| 93·40(10*R*) | 034·4 | 14·2 | | 7398·6 | 21·63 | 031·4 | 3·3 | | 01·6 |
| | | 381·1 | | | | | 381·3 | | |
| 3937·88(6) | 25387·3 | | | | 3183·96 | 31398·6 | | | |
| 35·72(8*R*) | 401·2 | 13·9 | | | 83·16 | 406·4 | 7·8 | | |
| | | 181·5 | | | | | 182·0 | | |
| 3909·92(8*R*) | 25568·8 | | | | 3165·60 | 31580·6 | | | |
| 3596·33 | 27798·3 | | (4) | 4634·6 | — | — | | (9) | 1134·2 |
| 93·20(4*r*) | 822·7 | 24·4 | | 4610·4 | 3193·97 | 31300·2 | | | 32·8 |
| 79·67(4*R*) | 927·7 | 105·0 | | 4505·3 | 93·91 | 300·8 | 0·6 | | 32·2 |
| | | 381·1 | | | | | 383·2 | | |
| 3547·70 | 28179·5 | | | | 3155·67 | 31680·1 | | | |
| 44·66(6*R*) | 203·6 | 24·1 | | | ‡ 55·34 | 683·4 | 3·3 | | |
| | | 181·6 | | | | | 181·3 | | |
| 3524·97(6*R*) | 28361·1 | | | | 3137·70 | 31861·4 | | | |
| *3421·48 | 29218·9 | | (5) | 3213·8 | — | — | | (10) | 932·9 |
| 21·01 | 222·9 | 4·0 | | 10·1 | †3173·72 | 31499·7 | | | |
| 20·32(4*R*) | 228·8 | 5·9 | | 04·2 | † 73·69 | 500·0 | 0·3 | | |
| | | 381·2 | | | | | 381·8 | | |
| 3377·39 | 29600·3 | | | | — | — | | | |
| 76·98(4*R*) | 603·9 | 3·6 | | | 3135·72 | 31881·5 | | | |
| | | 181·6 | | | | | 181·9 | | |
| 3356·80(6*R*) | 29781·9 | | | | 3117·94 | 32063·4 | | | |
| — | — | | (6) | 2351·2 | — | — | | (11) | 781·7 |
| 3323·06 | 30084·3 | | | 48·7 | — | — | | | |
| 22·80(4*r*) | 086·7 | 2·4 | | 46·3 | 3158·54 | 31651·1 | | | |
| | | 381·0 | | | | | 380·5 | | |
| 3281·77 | 30462·8 | | | | — | — | | | |
| 81·50(4*r*) | 465·3 | 2·5 | | | 3121·02 | 32031·6 | | | |
| | | 181·8 | | | | | | | |
| †3262·30(2*r*) | 30644·6 | | | | — | — | | | |
| — | — | | (7) | 1790·5 | — | — | | (12) | 664·7 |
| †3262·24 | 30645·2 | | | 88·0 | — | — | | | |
| 61·96 | 647·8 | 2·6 | | 85·2 | 3146·90 | 31768·3 | | | |
| | | 380·8 | | | | | 380·6 | | |
| 3222·44 | 31023·6 | | | | — | — | | | |
| † 22·19 | 026·0 | 2·4 | | | 3109·63 | 32148·9 | | | |
| | | 181·4 | | | | | | | |
| 3203·70 | 31205·0 | | | | — | — | | | |
| | | | | | 3137·80 | 31860·6 | | (13) | 572·4 |
| | | | | | 3130·6 | 31934 | | (14) | 499 |

* Much too strong; perhaps not a member of this series.

† These lines somewhat doubtful, as they are not clearly resolved.

‡ This may not belong to the series; triplet irregular.

## Ba Singlets.

**Principal. $1S—mP$.**
$1S=42029·4$.

| λ, Int. | ν | $m$ | $mP$ |
|---|---|---|---|
| 5535·53(10*R*) | 18060·2 | (1) | 23969·2 |
| 3071·59(6*R*) | 32547·2 | (2) | 9482·2 |
| 2702·65(4*R*) | 36989·9 | (3) | 5039·5 |
| 2596·68(4*R*) | 38499·5 | (4) | 3529·9 |
| 2543·2 | 39308 | (5) | 2721 |
| *2500·2 | 39985 | (6) | 2044 |
| *2473·1 | 40423 | (7) | 1606 |

**Sharp. $1P—mS$.**
$1P=23969·2$.

| λ, Int. | ν | $m$ | $mS$ |
|---|---|---|---|
| —5535·53(10*R*) | —18060·2 | (1) | 42029·4 |
| 13207 | 7569·8 | (2) | 16399·4 |

**Fundamental. $1D—mF$.**
$1D=30634·1$.

| λ, Int. | ν | $m$ | $mF$ |
|---|---|---|---|
| 5826·29(8*R*) | 17158·9 | (2) | 13475·2 |
| 4080·93 | 24497·4 | (3) | 6136·7 |
| 3789·74 | 26397·7 | (4) | 4254·4 |

**Combination. $1D—mP$.**

| λ, Int. | ν | $m$ | ν calc. |
|---|---|---|---|
| 15000·4 | 6664·9 | (1) | 6664·9 |
| 4726·46(8*R*) | 21151·7 | (2) | 21151·9 |
| ‡3905·98(2) | 25594·7 | (3) | 25594·6 |
| 3688·35(2) | 27104·5 | (4) | 27104·2 |

**Combination. $1S—mF$.**

| λ, Int. | ν | $m$ | ν calc. |
|---|---|---|---|
| 3501·12(10*R*) | 28554·3 | (2) | 28554·2 |
| 2785·26(8*n*) | 35893·0 | (3) | 35892·7 |
| 2646·50 | 37774·8 | (4) | 37775·0 |

**Diffuse. $1P—mD$.**
$1P=23969·2$.

| λ | ν | $m$ | $mD$ |
|---|---|---|---|
| —15000·4 | —6664·9 | (1) | 30634·1 |
| ?9831·7 | 10168·8 | (2) | 13800·4 |
| ?6233·59 | 16038·2 | (3) | 7931·0 |
| ?5267·03 | 18981·4 | (4) | 4987·8 |
| ?4877·69 | 20496·6 | (5) | 3472·6 |
| ?4663·60 | 21437·5 | (6) | 2531·7 |

**Combination. $2S—mP$.**

| λ, Int. | ν | $m$ | ν calc. |
|---|---|---|---|
| —— | —— | (2) | [6917·2] |
| 8799·70(2*n*) | 11360·9 | (3) | 11359·9 |
| 7766·80(2) | 12871·8 | (4) | 12869·5 |

**Other Combinations.**

| λ, Int. | ν | ν calc. |
|---|---|---|
| †9527·0 | 10493·6 | $1P—2F=10494·0$ |
| 3900·37(4*n*) | 25631·5 | $1S—2S=25630·0$ |

**Ba Inter-Combinations.**

| λ, Int. | ν | ν calc. |
|---|---|---|
| 7911·36(6) | 12637·1 | §$1S—1p_2=12636·6$ |
| 3244·20 | 30816·6 | §$1S—2p_2=30815·2$ |
| 11304·20 | 8844·1 | $1d'—1P=8844·9$ |
| ‡4284·90 | 23331·2 | $1d'—2P=23331·9$ |
| 3599·40 (6) | 27774·9 | $1d'—3P=27774·6$ |
| 3413·84 | 29284·3 | $1d'—4P=29284·2$ |

* Not positively identified as belonging to this series.
† Very faint line.
‡ Abnormally faint.
§ This series is strong at low temperatures.

The less refrangible components of the second, third, and fourth pairs of the sharp series lead to the formula

$$\sigma_1(m)=58712·5-4N/(m+1·438086-0·108104/m)^2$$

This gives the first line as —22099·4 in place of the observed —21952·4, and the fifth as 48057 in place of the observed 47999.

The limits assigned to the fundamental series follow the usual rules, but are considerably different from those independently calculated from the observed lines, namely, 71120·5 and 71696·4.

## $Ba^+$ Doublets.

**Principal.** $1\sigma - m\pi$. $1\sigma = 80664{\cdot}9$.

| λ, Int. | ν | Δν | *m* | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 4554·04 (10*R*) | 21952·4 | 1690·9 | (1) | 58712·5 |
| 4934·10 (9*R*) | 20261·5 | | | 60403·4 |

**Sharp.** $1\pi - m\sigma$. $1\pi_1 = 58712{\cdot}5$ ; $1\pi_2 = 60403{\cdot}4$.

| λ, Int. | ν | Δν | *m* | $m\sigma$ |
|---|---|---|---|---|
| —4554·04 (10*R*) | —21952·4 | 1690·9 | (1) | 80664·9 |
| —4934·06 (9*R*) | —20261·5 | | | |
| 4899·97 (8) | 20402·6 | 1690·9 | (2) | 38309·9 |
| 4524·95 (7) | 22093·5 | | | |
| 2771·35 (6) | 36072·8 | 1690·6 | (3) | 22639·8 |
| 2647·28 (4) | 37763·4 | | | |
| 2286·11 | 43728·9 | 1691 | (4) | 14983 |
| 2201·1 | 45420 | | | |
| 2082·7 | 47999 | | (5) | 10714 |

**Fundamental.** $1\delta - m\varphi$. $1\delta = 68097{\cdot}6$ ; $1\delta' = 68674{\cdot}3$.

| λ, Int. | ν | Δν | *m* | $m\varphi$ |
|---|---|---|---|---|
| 2335·25 (8*R*) | 42808·8 | 576·7 | (3) | 25288·8 |
| 2304·21 (8*R*) | 43385·5 | | | |
| 1869·2 | 53499 | | (4) | 14602 |
| 1849·5 | 54068 | | | |
| 1694·3 | 59021 | | (5) | 9077 |
| 1677·9 | 59598 | | | |

**Diffuse.** $1\pi - m\delta$. $1\pi_1 = 58712{\cdot}5$ ; $1\pi_2 = 60403{\cdot}4$.

| λ, Int. | ν | Δν | *m* | $m\delta', \delta$ |
|---|---|---|---|---|
| —10035·6 | — 9961·8 | 576·7 | (1) | 68674·3 |
| —10652·4 | — 9385·1 | | | 097·6 |
| | | 1689·1 | | |
| —12084·8 | — 8272·7 | | | |
| 4166·02 (4) | 23997·0 | 205·3 | (2) | 34715·5 |
| 4130·68 (8*R*) | 24202·3 | | | 510·2 |
| | | 1690·9 | | |
| 3891·79 (6*R*) | 25687·9 | | | |
| 2641·39 (4) | 37847·5 | 94·7 | (3) | 20865·8 |
| 2634·80 (7) | 37942·2 | | | 770·3 |
| | | 1689·3 | | |
| 2528·51 (5) | 39536·8 | | | |
| 2235·4 | 44721 | 54 | (4) | 13991 |
| 2232·7 | 44775 | | | 938 |
| | | 1691 | | |
| 2154·0 | 46412 | | | |
| —— | —— | | | |
| 2054·9 | 48649 | | (5) | 10109 |
| | | | | 064 |
| 1987·7 | 50294 | | | |

*Unclassified Pair.**

| λ, Int. | ν | Δν |
|---|---|---|
| 5853·70 (8) | 17078·5 | 1690·9 |
| 6496·90 (8) | 15387·6 | |

* Zeeman effect is of δ type.

## Radium.

Ra. At. wt. = 226·4 ; At. No. = 88.

Measurements of the spark spectrum of radium, between wave-lengths 6487 and 2709, were made by Runge and Precht,* of the arc and spark by Exner and Haschek,† and of the spark spectrum by Crookes.‡ The spark spectrum may, of course, include arc lines, just as the arc often includes spark lines.

The series of arc lines have not yet been satisfactorily traced. Analogy with the other elements of the alkaline earth group indicates that a triplet system and a

* Ann. d. Ph., **14**, 418 (1904).
† Wien. Ber., **120**, IIA, 967 (1911).
‡ Proc. Roy. Soc., **72**, 295, 413 (1903).

system of singlets may be expected. Hicks* has attempted to find the triplets, and has suggested an arrangement which gives separations 2050 and 832 ?, but the relative intensities and general fragmentary character of the suggested triplets leave the question very doubtful. A further attempt has been made by the Misses Anslow and Howell,† who proceeded on the basis of $\Delta\nu$=about 3060 for the separation of the extreme components of the triplets as deduced from the spectra of calcium, strontium and barium. Attention is drawn to a number of possible triplets with $\Delta\nu_1$, $\Delta\nu_2$=2016·64 and 1036·15, giving 3052·79 for the extreme members. These intervals, however, are averages, and the individual differences seem to vary more than the probable errors of measurement. The wave-numbers were not corrected to vacuum in this investigation, but when this correction is made the results are not sufficiently improved to establish confidence. Furthermore, the intensities of the components of the triplets are irregular, and the suggested satellites call for further investigation.

There is a strong line in the flame spectrum at $\lambda$ 4825·94 I.A.

## Ionised Radium ($Ra^+$).

Some of the lines of the spark spectrum were identified by Ritz as forming pairs analogous with corresponding pairs of Ca, Sr, and Ba.‡ These may now be certainly regarded as enhanced lines, although their behaviour in the arc has not been investigated. The lines are not sufficiently numerous to permit the calculation of satisfactory formulæ, but by assuming the constant for these series to be $4N$, and using a simple Rydberg formula, the limit for the less refrangible components of the sharp series is found to be about 57863. Hicks, however, has found reason to believe that the true limit is nearer to 56653·23, and this has been adopted in the following table for the known lines of $Ra^+$ :—

### $Ra^+$ Doublets.

Principal. $1\sigma - m\pi$. $1\sigma = 82862{\cdot}05$.

| λ, Int. | ν | Δν | $m$ | $m\pi_{1,2}$ |
|---|---|---|---|---|
| 3814·43 (100) | 26208·82 | 4857·21 | (1) | 56653·23 |
| 4682·18 (50) | 21351·61 | | | 61510·44 |

Diffuse. $1\pi - m\delta$. $1\pi_1 = 56653{\cdot}23$ ; $1\pi_2 = 61510{\cdot}44$.

| λ, Int. | ν | Δν | $m$ | $m\delta', \delta$. |
|---|---|---|---|---|
| 4436·32 (20) | 22534·90 | 496·56 | (2) | 34118·1 |
| 4340·67 (50) | 23031·46 | | | 33621·77 |
| | | 4857·59 | | |
| 3649·60 (50) | 27392·49 | | | |

Sharp. $1\pi - m\sigma$. $1\pi_1 = 56653{\cdot}23$ ; $1\pi_2 = 61510{\cdot}44$.

| λ, Int. | ν | Δν | $m$ | $m\sigma$ |
|---|---|---|---|---|
| —3814·43 (100) | —26208·82 | 4857·21 | (1) | 82862·05 |
| —4682·18 (50) | —21351·61 | | | |
| 5813·63 (15) | 17196·20 | 4857·30 | (2) | 39456·98 |
| 4533·16 (10) | 22053·50 | | | |

Fues§ gives the limits as $1\sigma$=80,000, $1\pi_1$=53785, $1\pi_2$=58645.

* Phil. Trans., A. **212**, 64 (1913).
† Proc. Nat. Acad. Sci., Wash., **3**, 409 (1917).
‡ Phys. Zeit., **16**, 521 (1908).
§ Ann. d. Phys., **63**, 17 (1920).

# CHAPTER XV.

## GROUP IIB.—ZINC, CADMIUM, AND MERCURY.

The elements zinc, cadmium, and mercury form a second branch of Group II. of the periodic system, and their spectra have a general resemblance to those of the alkaline earth metals, which form the first branch. Thus, the arc spectrum in each case comprises a triplet system and a singlet system, with combinations and inter-combinations. The spectra of the ionised elements have not been completely investigated, but it is probable that they yield doublets as in the case of the alkaline earth metals.

The elements, zinc, cadmium, and mercury, however, while showing the usual atomic weight relationship among themselves, are not united in this way with the alkaline earth metals.

The sharp and diffuse series of triplets were identified by Rydberg, and by Kayser and Runge, and the work of Paschen* subsequently led to a knowledge of the principal series and of the single line systems, in addition to numerous combinations. A further important contribution was made in Paschen's laboratory by K. Wolff,† who traced the principal series of singlets in the Schumann region, and obtained wave-lengths which appear to be of remarkable accuracy.

The spectra of zinc and cadmium in the Schumann region have also been observed by McLennan, Ainslie and Fuller.‡

The most complete lists of wave-lengths are those given by Kayser and Runge. These have been supplemented in the ultra-violet for Zn and Cd by Huppers§ and by Eder.||

A partial revision of wave-lengths for Zn and Cd, based on photographs of vacuum arc spectra, has been made by Saunders,¶ and the new wave-lengths have been adopted in the tables which follow.

### ZINC.

Zn. At. wt. = 65·38 ; At. No. = 30.

The wave-lengths of the principal series of triplets, and of all the lines less refrangible than $\lambda$4810, have been adopted from the observations by Paschen. For the sharp and diffuse series the revision and extension by Saunders have been utilised. The remaining wave-lengths are mostly from the lists of Kayser and Runge and of Huppers, except in the region of short wave-lengths. The adopted limits of the series are as determined by Saunders.

Apart from lines which are probably due to impurities of lead and tin, there are very few tabulated lines which do not find places in one or other of the series. The combination line $1S-2D$, at 1601·09, has not previously been recognised as such.

The "single line" spectrum of zinc, as observed by McLennan,** is represented by the prominent line $\lambda$ 3075·88, being the inter-combination $1S-1p_2$.

* Ann. d. Phys., **29**, 625 (1909) ; **30**, 747 (1909) ; **35**, 860 (1911) ; **40**, 602 (1913).
† Ann. d. Phys., **42**, 825 (1913).
‡ Proc. Roy. Soc., A. **95**, 316 (1919).
§ Zeit. Wiss. Phot., **13**, 46 (1914).
|| *Ibid.*, **13**, 20 (1914) ; **14**, 137 (1915).
¶ Privately communicated.
** Proc. Roy. Soc., A. **91**, 485 (1915).

## Zn Triplets.

**Principal.** $1s—mp$. $1s=22094\cdot4$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| –4810·53(10*R*) | —20781·9 | 388·9 | (1) | 42876·3 |
| –4722·16(10*R*) | —21170·8 | 189·8 | | 43265·2 |
| –4680·20(10*R*) | — 360·6 | | | 455·0 |
| 13054·89 | 7657·9 | 56·2 | (2) | 14436·5 |
| 151·50 | 01·7 | 26·7 | | 492·7 |
| 197·79 | 7575·0 | | | 519·4 |
| 6928·33(8) | 14429·5 | 21·1 | (3) | 7664·9 |
| 38·48(6) | 408·4 | 19·8 | | 86·0 |
| 43·22(4) | 398·6 | | | 95·8 |
| 5772·00(10) | 17320·2 | 10·3 | (4) | 4774·2 |
| 75·43(8) | 309·9 | 4·7 | | 84·5 |
| 77·02(6) | 305·2 | | | 89·2 |
| 5308·51(8) | 18832·4 | 5·6 | (5) | 3262·0 |
| 10·11(6) | 826·8 | 2·6 | | 67·6 |
| 10·84(4) | 824·2 | | | 70·2 |
| 5068·53(4) | 19724·1 | 3·7 | (6) | 2370·3 |
| 69·49(2) | 720·4 | 1·9 | | 74·0 |
| 69·98(0) | 718·5 | | | 75·9 |

**Sharp.** $1p—ms$. $1p_1=42876\cdot3$ ; $1p_2=43265\cdot2$ ; $1p_3=43455\cdot0$.

| λ, Int. | ν | Δν | $m$ | $ms$. |
|---|---|---|---|---|
| 4810·53(10*R*) | 20781·9 | 388·9 | (1) | 22094·4 |
| 4722·16(10*R*) | 21170·8 | 189·8 | | |
| 4680·20(10*R*) | 360·6 | | | |
| 3072·07(10*R*) | 32541·9 | 388·7 | (2) | 10334·4 |
| 35·81(10*R*) | 930·6 | 190·1 | | |
| 18·38(8*r*) | 33120·7 | | | |
| 2712·48(8*R*) | 36855·8 | 390·1 | (3) | 6020·5 |
| 2684·06(8*R*) | 37245·9 | 189·9 | | |
| 70·44(6*r*) | 435·8 | | | |
| 2567·80(6*r*) | 38932·2 | 390·2 | (4) | 3944·1 |
| 42·32(6*r*) | 39322·4 | 190·0 | | |
| 30·09(2*r*) | 512·4 | | | |
| 2493·32(4*n*) | 40095·1 | 390·2 | (5) | 2781·2 |
| 69·38(2*r*) | 485·3 | 190·2 | | |
| 57·80(1*r*) | 674·5 | | | |
| 2449·72(1) | 40808·3 | 388·5 | (6) | 2068·0 |
| 26·63(1) | 41196·8 | 190·1 | | |
| 15·48(1) | 386·9 | | | |
| 2421·82 | 41278·7 | 388·6 | (7) | 1597·6 |
| 2399·23 | 667·3 | 190·7 | | |
| 88·30 | 858·0 | | | |
| 2402·82 | 41605·5 | | (8) | 1270·8 |

* Observations discordant, and enhanced line involved.

**Diffuse.** $1p—md$. $1p_1=42876\cdot3$ ; $1p_2=43265\cdot2$ ; $1p_3=43455\cdot0$.

| λ, Int. | ν | Δν | $m$ | $md''$, $d'$, $d$ |
|---|---|---|---|---|
| 3345·96(4) | 29878·2 | 4·0 | (2) | 12997·6 |
| 45·51(8*R*) | 882·2 | 5·4 | | 994·2 |
| 44·91(10*R*) | 887·6 | 389·4 | | 988·7 |
| 3302·91(8*R*) | 30267·6 | 3·2 | | |
| 02·56(8*R*) | 270·8 | 190·3 | | |
| 3282·28(8*R*) | 30457·9 | | | |
| —— | —— | | (3) | 7187·0 |
| 2801·07(7) | 35690·2 | 2·2 | | 85·9 |
| 00·90(8) | 692·4 | | | 83·9 |
| 2770·95(6*R*) | 36078·0 | 1·5 | | |
| 70·84(8*R*) | 079·5 | 190·2 | | |
| 2756·43(6*R*) | 36268·2 | | | |
| | | | | *md* |
| 2608·55(8*R*) | 38323·0 | 389·4 | (4) | 4553·3 |
| 2582·38(8*R*) | 712·4 | 189·5 | | |
| 69·80(6*R*) | 901·9 | | | |
| 2515·81(6) | 39737·6 | 387·1 | (5) | 3138·7 |
| 2491·48(6) | 40124·7 | 189·9 | | |
| 79·74(4) | 314·6 | | | |
| 2463·47(4) | 40580·8 | 388·5 | (6) | 2295·5 |
| 40·11(4) | 969·3 | | | |
| * —— | — | | | |
| 2430·79(1) | 41126·4 | 387·0 | (7) | 1749·9 |
| 08·13(1) | 513·4 | 190·1 | | |
| 2397·15 | 703·5 | | | |
| 2409·06 | 41497·4 | 386·9 | (8) | 1378·9 |
| 2386·80 | 884·3 | 190·1 | | |
| 76·01 | 42074·4 | | | |
| 2393·85 | 41761·0 | 388·5 | (9) | 1115·3 |
| 71·78 | 42149·5 | 193·2 | | |
| 60·96 | 342·7 | | | |
| 2382·22 | 41964·8 | | (10) | 911·5 |
| 60·96 | 42342·7 | | | |
| 2374·36 | 42103·7 | | (11) | 707·6 |
| 2367·72 | 42221·9 | | (12) | 654·4 |

**Fundamental.** $2d—mf$. $2d=12988\cdot7$ ; $2d'=12994\cdot2$ ; $2d''=12997\cdot6$.

| λ | ν | Δν | $m$ | $mf$ |
|---|---|---|---|---|
| 16498·6 | 6059·5 | 3·1 | (3) | 6931·3 |
| 490·3 | 6062·6 | 2·4 | | |
| 483·7 | 6065·0 | | | |
| | | | (4) | [4442·3] |

## Zn TRIPLETS—*Continued.*

COMBINATION. $1p—mf$.
$1p_1=42876·3$ ; $1p_2=43265·2$ ; $1p_3=43455·0$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 2781·23 (4*v*) | 35944·1 | $1p_1—3f=35945·0$ |
| 51·39 (2*v*) | 36334·6 | $1p_2—3f=36333·9$ |
| 36·86 (2*n*) | 527·4 | $1p_3—3f=36523·7$ |
| 2600·94 (2*n*) | 38436·1 | $1p_1—4f=38434·0$ |
| 2575·06 (2*n*) | 822·4 | $1p_2—4f=822·9$ |
| 62·61 (2*n*) | 39011·0 | $1p_3—4f=39012·7$ |

COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| 24045·7 | 4157·6 | $2p_2—2s=4158·3$ |
| 13792·4 | 7248·4 | $2p_1—3d'=7250·6$ |
| 13784·8 | 7252·4 | $2p_1—3d=7252·6$ |
| 10979·4 | 9105·5 | $1s—2d=9105·7$ |
| 3515·11(1*n*) | 28440·5 | $1p_1—2p_1=28439·8$ |

## Zn SINGLETS.

PRINCIPAL. $1S—mP$.
$1S=75766·8$.

| λ, Int. | ν | *m* | *mP* |
|---|---|---|---|
| * 2138·61 (8*R*) | 46745·1 | (1) | 29021·7 |
| † 1589·76 (10) | 62902 | (2) | 12857·9‡ |
| † 1457·56 (8) | 68608 | (3) | 7160·6‡ |
| † 1404·19 (4) | 71215 | (4) | 4559·1‡ |
| † 1376·87 (2) | 72629 | (5) | 3141·7‡ |

SHARP. $1P—mS$.
$1P=29021·7$.

| λ, Int. | ν | *m* | *mS* |
|---|---|---|---|
| —2138·61 (8*R*) | —46745·1 | (1) | 75766·8 |
| 11055·4 | 9043·0 | (2) | 19978·7 |
| 5182·0 (5) | 19292·2 | (3) | 9729·5 |
| 4298·38 (2) | 23258·0 | (4) | 5763·7 |
| § 3965·7 | 25209·2 | (5) | 3812·5 |
| § 3799·4 | 26312·3 | (6) | 2709·4 |

DIFFUSE. $1P—mD$.
$1P=29021·7$

| λ, Int. | ν | *m* | *mD* |
|---|---|---|---|
| 6362·37 (10) | 15713·1 | (2) | 13308·6 |
| 4629·88 (8*r*) | 21592·8 | (3) | 7428·9 |
| § 4113·6 | 24302·5 | (4) | 4719·2 |
| § 3883 ±2 | 25746 ∓13 | (5) | 3276 ±13 |

COMBINATION. $2S—mP$.
$2S=19978·7$.

| λ | ν | *m* | *mP* |
|---|---|---|---|
| —11055·4 | —9043·0 | (1) | 29021·7 |
| 14039·5 | 7120·8 | (2) | 12857·9 |
| 7799·33 (6) | 12818·1 | (3) | 7160·6 |
| 6479·24 (5) | 15429·6 | (4) | 4559·1 |
| 5937·67 (3) | 16837·0 | (5) | 3141·7 |
| 5654·39 (1) | 17680·5 | (6) | 2298·2 |
| 5485·98 (1) | 18223·2 | (7) | 1755·5 |

COMBINATION.

| λ, Int. | ν | ν calc. |
|---|---|---|
| † 1601·09 (4) | 62457 5 | $1S—2D=62458·2$ |

Zn INTER-COMBINATIONS.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 15682·1 | 6375·0 | $2D—3f=6377·3$ |
| 6239·22 (6) | 16023·2 | $1P—2d''=16024·1$ |
| 6238·00 (8) | 16026·4 | $1P—2d'=16027·5$ |
| ‖3075·88 (8*R*) | 32501·6 | $1S—1p_2=32501·6$ |
| 4292·86 (2) | 23288·0 | $1p_2—2S=23286·5$ |
| †1632·11 (4) | 61270·4 | $1S—2p_2=61274·1$ |

*Unclassified Lines of* Zn.

| λ, Int. | ν |
|---|---|
| 10970·7 | 9113·2 |
| 7478·75 (6) | 13367·5 |
| 6470·98 (4) | 15449·3 |
| 6102·17 (2) | 16383·1 |
| 6022 (1) | 16601 |
| ?4101·79 (2) | 24372·8 |
| 3739·97 (4) | 26730·6 |
| 2623·78 (1) | 38101·6 |
| ?2393·81 | 41761·7 |
| ?2063·8 | 48438 |

| Wolff. | | McLennan, Ainslie and Fuller. | |
|---|---|---|---|
| λ vac. | ν | λ vac. | ν |
| 1649·87 (5) | 60610·8 | | |
| | | 1510·4 (1) | 66207 |
| | | 1491·5 (1) | 67047 |
| 1486·20 (5) | 67285·7 | 1486·2 (6) | 67286 |
| | | 1478·5 (2) | 67636 |
| 1476·01 (2) | 67750·2 | 1477·6 (4) | 67677 |
| 1474·67 (3) | 67811·8 | | |
| 1450·82 (1) | 68926·5 | 1451·1 (4) | 69915 |
| | | 1445·0 (3) | 69204 |

* Eder's λ in spark is 2138·55.
† Wolff λ vac.
‡ Determined from combination $2S—mP$.
§ New values by Saunders.
‖ Used for calculation of $1S$.

## Ionised Zinc ($Zn^+$).

Certain pairs of lines in the spectrum of zinc, with a mean separation of 876, were noted by Rydberg, and further attention was directed to them by Paschen, who also observed their behaviour in the magnetic field.

The lines in question are definitely enhanced lines, and there can be no doubt that they originate in the ionised element. The magnetic resolutions suggest that one of the pairs is of the principal, and the other of the sharp series type. A third pair, in the orange, noted by Paschen as having the same separation, gives a magnetic resolution of the diffuse series type. On the basis of $N$ for the series constant, Paschen assigned one pair to $0{\cdot}5\sigma-1\pi_{1,2}$ and the other to $1\pi_{1,2}-1{\cdot}5\sigma$, in the notation of Ritz. When $4N$ is adopted for the series constant, and in the notation of this Report, these become respectively $1\sigma-1\pi_{1,2}$ and $1\pi_{1,2}-2\sigma$. The lines are too few to permit a trustworthy calculation of limits, but approximate values, as shown below, have been derived by the use of Rydberg's table, with $4N$ for constant.*

### $Zn^+$ Doublets.

| Principal. $1\sigma-m\pi$. $1\sigma=147{,}544$. | | | | | Sharp. $1\pi-m\sigma$. $1\pi_1=98190$ ; $1\pi_2=99062$. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| λ | ν | Δν | $m$ | $m\pi_{1,2}$ | λ | ν | Δν | $m$ | $m\sigma$ |
| *2025·49<br>61·96 | 49354·7<br>48482·5 | 872·2 | (1) | 98190<br>99062 | —2025·49<br>— 61·96 | —49354·7<br>—48482·5 | 872·2 | (1) | 147,544 |
| *Unclassified Pair, Diffuse Type.* | | | | | †2558·01<br>02·03 | 39081·1<br>955·7 | 874·6 | (2) | 59,109 |
| λ | ν | Δν | | | | | | | |
| 6214·65<br>5894·43 | 16086·6<br>960·5 | 873·9 | | | * λ Eder.<br>† λ Huppers. | | | | |

There are numerous other enhanced lines of zinc, especially in the ultra-violet, and further investigation of the series is needed. Attention should be specially drawn to the pair of lines 4923·98(10) and 4911·63(10), with wave-numbers 20303·1 and 20354·2. There is an analogous pair in cadmium, and since they do not occur in the true arc spectrum,† it is possible that they correspond with 4481 of magnesium, and may be members of a series of the fundamental type.

## Cadmium.

Cd. At. wt.=112·4 ; At. No.=48.

The authorities for wave-lengths are generally the same as for zinc, and the adopted limits are as communicated by Saunders.

The "single line" or "resonance" spectrum, as observed by McLennan, is represented by the combination line $1S-1p_2$, λ3261·04.

* Fues gives $1\pi_1=109650$, $1\pi_2=110{,}520$, $1\sigma=159{,}000$ (Ann. d. P., **63**, 18, 1920).
† Fowler and Payn, Proc. Roy. Soc., **72**, 255, Plate 14 (1903).

## Cd Triplets.

**Principal.** $1s—mp$. $1s=21054\cdot7$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| —5085·88 (10*R*) | —19656·8 | 1171·1 | (1) | 40711·5 |
| —4799·91 (10*R*) | —20827·9 | 541·9 | | 41882·6 |
| —4678·19 (10*R*) | —21369·8 | | | 42424·5 |
| 13979·22 | 7151·6 | 174·1 | (2) | 13903·1 |
| 14327·99 | 6977·5 | 70·7 | | 14077·2 |
| 14474·62 | 6906·8 | | | 14147·9 |
| 7346·2 (10) | 13608·7 | 71·5 | (3) | 7446·0 |
| 85·0 (9) | 537·2 | 25·4 | | 7517·5 |
| 98·9 (5) | 511·8 | | | 7542·9 |
| 6099·18 (8) | 16391·1 | 33·1 | (4) | 4663·6 |
| 6111·52 (6) | 358·0 | 12·5 | | 4696·7 |
| 6116·19 (4) | 345·5 | | | 4709·2 |
| 5598·77 (6) | 17856·1 | 18·8 | (5) | 3198·6 |
| 5604·68 (4) | 837·3 | 6·9 | | 3217·4 |
| 5605·85 (2) | 830·4 | | | 3224·3 |
| 5339·50 (1) | 18723·2 | | (6) | 2331·5 |

**Sharp.** $1p—ms$. $1p_1=40711\cdot5$; $1p_2=41882\cdot6$; $1p_3=42424\cdot5$.

| λ, Int. | ν | Δν | $m$ | $ms$ |
|---|---|---|---|---|
| 5085·88 (10*R*) | 19656·8 | 1171·1 | (1) | 21054·7 |
| 4799·91 (10*R*) | 20827·9 | 541·9 | | |
| 4678·19 (10*R*) | 21369·8 | | | |
| 3252·52 (8*r*) | 30736·5 | 1170·6 | (2) | 9975·6 |
| 3133·19 (8*r*) | 31907·1 | 541·2 | | |
| 3080·93 (6*r*) | 32448·3 | | | |
| 2868·26 (6*r*) | 34854·1 | 1171·3 | (3) | 5857·3 |
| 2775·00 (6*r*) | 36025·4 | 541·8 | | |
| 2733·88 (4*r*) | 567·2 | | | |
| 2712·40 (6*r*) | 36857·1 | 1168·0 | (4) | 3856·6 |
| 2629·06 (4*r*) | 38025·1 | 541·5 | | |
| 2592·14 (2*r*) | 566·6 | | | |
| 2632·25 (2*r*) | 37979·1 | 1170·6 | (5) | 2732·9 |
| 2553·53 | 39149·7 | 541·3 | | |
| 2518·70 | 691·0 | | | |
| 2585·07 | 38672·1 | 1173·8 | (6) | 2037·6 |
| 2508·91 | 39845·9 | 541·8 | | |
| 2475·25 | 40387·7 | | | |
| 2554·51 | 39134·7 | 1171·1 | (7) | 1576·8 |
| 2480·28 | 40305·8 | | | |
| — | — | | | |
| 2533·91 | 39452·9 | 1173·3 | (8) | 1257·0 |
| 2460·72 | 40626·2 | | | |
| — | — | | | |

**Diffuse.** $1p—md$. $1p_1=40711\cdot5$; $1p_2=41882\cdot6$; $1p_3=42424\cdot5$.

| λ, Int. | ν | Δν | $m$ | $md''$, $d'$, $d$ |
|---|---|---|---|---|
| 3614·43 (4) | 27659·0 | 11·8 | (2) | 13052·4 |
| 12·89 (8*R*) | 670·8 | 18·2 | | 13040·7 |
| 10·51 (10*R*) | 689·0 | | | 13022·5 |
| | | 1171·1 | | |
| 3467·61 (8*R*) | 28830·1 | 11·9 | | |
| 66·18 (10*R*) | 842·0 | | | |
| | | 542·2 | | |
| 3403·60 (10*R*) | 29372·3 | | | |
| 2981·89 (1) | 33526·0 | 6·2 | (3) | 7185·3 |
| 81·34 (4*R*) | 532·2 | 8·0 | | 7179·5 |
| 80·63 (8*R*) | 540·2 | | | 7171·3 |
| | | 1171·3 | | |
| 2881·23 (4*R*) | 34697·3 | 5·5 | | |
| 80·77 (8*R*) | 702·8 | | | |
| | | 542·1 | | |
| 2836·90 (8*R*) | 35239·4 | | | |
| — | — | | (4) | 4549·9 |
| 2764·19 (2*R*) | 36166·2 | | | 4546·3 |
| 63·89 (6*R*) | 170·2 | | | 4541·3 |
| — | — | | | |
| 2677·64 (8*d*) | 37335·2 | | | |
| 2639·50 (6*R*) | 37874·6 | | | |
| 2660·40 (4*r*) | 37577·2 | | (5) | 3139·2 |
| 2580·27 (2*n*) | 38744·1 | | | 3138·5 |
| 44·72 (2*n*) | 39285·3 | | | 3134·5 |
| 2602·18 (2*n*) | 38417·8 | | (6) | 2294·5 |
| 2525·30 (1*n*) | 39587·3 | | | |
| 2491·16 | 40129·9 | | | |
| 2565·88 | 38961·3 | | (7) | 1751·3 |
| 2491·16 | 40129·9 | | | |
| 57·87 | 40673·4 | | | |
| 2541·64 | 39332·9 | | (8) | 1379·3 |
| 2468·25 | 40502·2 | | | |
| 35·58 | 41045·5 | | | |
| 2524·68 | 39597·1 | | (9) | 1114·3 |
| 2452·22 | 40767·1 | | | |
| 19·90 | 41311·4 | | | |
| 2512·37 | 39791·0 | | (10) | 920·3 |
| 2440·51 | 40962·6 | | | |
| 2502·99 | 39940·3 | | (11) | 771·6 |
| 2431·73 | 41110·5 | | | |
| 2495·88 | 40054·0 | | (12) | 658·1 |
| 25·04 | 41223·9 | | | |
| 2490·23 | 40144·8 | | (13) | 566·7 |

## Cd TRIPLETS—*Continued.*

FUNDAMENTAL. $2d—mf$.
$2d=13022{\cdot}5$ ; $2d'=13040{\cdot}7$ ; $2d''=13052{\cdot}4$.

| λ | ν | $m$ | $mf$ |
|---|---|---|---|
| 16482·2 | 6065·5 | | |
| 16433·8 | 6083·4 | (3) | 6957·1 |
| 16401·5 | 6095·4 | | |
| 11630·8 | 8595·6 | (4) | 4445·1 * |

COMBINATION. $1p—mf$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 2961·48 (4*v*) | 33757·1 | $1p_1—3f=33754{\cdot}4$ |
| 2862·30 (2*v*) | 34926·7 | $1p_2—3f=34925{\cdot}5$ |
| 2818·73 (1*v*) | 35466·5 | $1p_3—3f=35467{\cdot}4$ |
| 2756·78 (3*n*) | 36263·5 | $1p_1—4f=36266{\cdot}4$ |
| 2670·66 (3*n*) | 37432·9 | $1p_2—4f=37437{\cdot}5$ |
| 2632.26 (2*n*) | 37978·9 | $1p_3—4f=37979{\cdot}4$ |

OTHER COMBINATIONS.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 14852·9 | 6730·4 | $2p_1—3d = 6731{\cdot}8$ |
| 14474·6 | 6906·8 | $2p_2—3d = 6905{\cdot}9$ |
| 14329·6 | 6976·8 | $2p_3—3d = 6976{\cdot}6$ |
| 14354·5 | 6964·6 | $2p_3—3d'' = 6962{\cdot}6$ |
| 3729·06 (4*r*) | 26808·8 | $1p_1—2p_1=26808{\cdot}4$ |
| 3005·41 (1*r*) | 33263·7 | $1p_1—3p_1=33265{\cdot}5$ |
| 3595·49 (1*n*) | 27804·7 | $1p_2—2p_2=27805{\cdot}4$ |
| 2903·13 (1*n*) | 34435·9 | $1p_2—3p_1=34436{\cdot}6$ |
| 2908·74 (1*r*) | 34369·1 | $1p_2—3p_2=34365{\cdot}1$ |

* The term $4f$ is somewhat uncertain.

## Cd SINGLETS.

PRINCIPAL. $1S—mP$.
$1S=72538{\cdot}8$.

| λ, Int. | ν | $m$ | $mP$ |
|---|---|---|---|
| 2288·02 (10*R*) | 43692·2 | (1) | 28846·6 |
| *1669·29 (10) | 59905·7 | (2) | 12633·2 |
| *1526·85 (8) | 65494·3 | (3) | 7044·6 |
| *1469·39 (6) | 68055·5 | (4) | 4483·4 |
| *1440·18 (3) | 69435·8 | (5) | 3103·1 |
| *1423·23 (1) | 70262·7 | (6) | 2276·2 |

SHARP. $1P—mS$.
$1P=28846{\cdot}6$.

| λ, Int. | ν | $m$ | $mS$ |
|---|---|---|---|
| —2288·02 (10*R*) | —43692·2 | (1) | 72538·8 |
| 10394·7 | 9617·3 | (2) | 19229·3 |
| 5154·68 (6*r*) | 19394·5 | (3) | 9452·1 |
| 4306·82 (4*n*) | 23212·5 | (4) | 5634·1 |
| 3981·77 (2*r*) | 25107·4 | (5) | 3739·2 |
| †3818·5 | 26180·9 | (6) | 2665·7 |
| †3723·2 | 26851·0 | (7) | 1995·6 |

COMBINATIONS.

| λ | ν | ν calc. |
|---|---|---|
| * 1688·58 (2) | 59221·4 | $1S—1D=59219{\cdot}5$ |
| 39086·9 | 2557·7 | $3P—4P= 2557{\cdot}8$ |

DIFFUSE. $1P—mD$.
$1P=28846{\cdot}6$.

| λ, Int. | ν | $m$ | $mD$ |
|---|---|---|---|
| ‡6438·47 (10) | 15527·4 | (2) | 13319·2 |
| 4662·51 (8*r*) | 21441·7 | (3) | 7404·9 |
| †4140·5 | 24144·9 | (4) | 4701·7 |
| †3905·1 | 25600·3 | (5) | 3246·3 |

COMBINATION. $2S—mP$.
$2S=19229{\cdot}3$.

| λ | ν | $m$ | $mP$ |
|---|---|---|---|
| §—10394·7 | — 9617·3 | (1) | 28846·6 |
| 15154·8 | 6596·8 | (2) | 12632·5 |
| 8200·2 | 12191·5 | (3) | 7037·8 |
| 6778·10 | 14749·3 | (4) | 4480·0 |
| 6198·22 | 16129·2 | (5) | 3100·1 |
| 5895·8 | 16956·5 | (6) | 2272·8 |
| 5715·8 | 17490·5 | (7) | 1738·8 |
| ?5598·06 | 17858·4 | (8) | 1380·9? |

* λ vac., Wolff.
† Saunders.
‡ The fundamental line of the international system of wave-lengths.
§ λ Paschen (Trans. Int. Sol. Union, **4**, 81, 1913).

Cd SINGLETS—*Continued.*

| Cd INTER-COMBINATIONS. | | |
|---|---|---|
| λ, Int. | ν | ν calc. |
| 15713·5 | 6362·2 | $2D-3f=$ 6362·1 |
| 11268·4 | 8872·0 | $2D-4f=$ 8874·1 |
| 6329·97 (8) | 15793·5 | $1P-2d''=15794·2$ |
| 6325·19 (10) | 15805·4 | $1P-2d'=15805·9$ |
| 4615·39 | 21660·6 | $1P-3d''=21661·3$ |
| 4614·17 | 21666·3 | $1P-3d'=21667·4$ |
| 4114·5 | 24297·4 | $1P-4d''=24296·7$ |
| | | $1P-4d'=24300·3$ |
| 5297·64 (2) | 18871·1 | $1P-2s=18871·0$ |
| *1942·29 (6) | 51485·6 | $1S-1s=51484·1$ |
| †3261·04 (10) | 30656·2 | $1S-1p_2=30656·2$ |
| *1710·51 (3) | 58462·1 | $1S-2p_2=58461·6$ |
| *1537·83 (1) | 65026·7 | $1S-3p_2=65021·3$ |
| 4413·06 (6) | 22653·7 | $1p_2-2S=22653·3$ |
| 3082·68 | 32429·6 | $1p_2-3S=32430·5$ |
| 7132·1 | 14017·3 | $1s-3P=14016·9$ |
| 6031·39 | 16575·3 | $1s-4P=16574·7$ |
| 5568 | 17954·8 | $1s-5P=17954·6$ |
| 5324 | 18777·7 | $1s-6P=18781·9$ |
| 3649·59 (2r) | 27392·5 | $1p_1-2D=27392·3$ |
| 3499·94 (4r) | 28563·7 | $1p_2-2D=28563·4$ |

* λ vac., Wolff.

† Used in calculation of 1*S*.

‡ Dr. Catalan has suggested that this may be the combination $2p_2-3p_2$, giving $\nu=6559·7$.

§ The wave-number is 352·6 lower than that of the line $1S-1p_2$.

|| The wave-number is 351·9 lower than that of the line $1S-1P$.

¶ Other lines in the Schumann region have been recorded by McLennan, Ainslie and Fuller (Proc. Roy. Soc., A. **95**, 330, 1919).

*Unclassified Lines of* Cd. ¶

| λ, Int. | ν |
|---|---|
| ‡15257·3 | 6552·4 |
| 6128·66 (2) | 16312·3 |
| 5783·93 (4) | 17284·5 |
| 5637·22 (5) | 17734·3 |
| 4615·75 (2) | 21658·9 |
| 4511·34 (5) | 22160·2 |

| λ | ν | Δν |
|---|---|---|
| §3298·97 (4) | 30303·6 | |
| 2748·61 (2) | 36371·3 | |
| 2657·00 (2) | 37625·2 | |
| 2654·55 (1) | 37660·0 | |
| 2329·27 (10) | 42918·6 | |
| 2267·48 (5) | 44088·2 | 1169·6 |
| 2239·86 (5) | 44631·7 | 543·5 |

| λ | ν |
|---|---|
| ‖2306·61 (5) | 43340·3 |
| 2262·29 (1) | 44189·3 |
| 2230·40 (1) | 44820·9 |
| 2170·04 (1) | 46067·7 |

| λ vac. | ν |
|---|---|
| *1993·07 (1) | 50173·8 |
| *1682·12 (1) | 59448·8 |
| *1647·78 (2) | 60687·7 |
| *1571·40 (1) | 63637·5 |

## IONISED CADMIUM ($Cd^+$).

The spectrum of ionised cadmium is similar to that of zinc, and Paschen has suggested that one pair belongs to the principal and another to the sharp series. Limits have been calculated by the Rydberg formula on the supposition that the series constant is 4*N*; but they can only be regarded as roughly approximate.* The wave-lengths of the principal and sharp pairs are by Huppers; those of the unclassified pair by Eder.

* Fues gives $1\pi_1=103,880$, $1\pi_2=105,350$, $1\sigma=150,500$.

Cd+ DOUBLETS.

| PRINCIPAL. $1\sigma - m\pi$. $1\sigma = 140225{\cdot}7$. | | | | | SHARP. $1\pi - m\sigma$. $1\pi_1 = 93607{\cdot}2$; $1\pi_2 = 96090{\cdot}0$. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| λ, Int. | ν | Δν | $m$ | $m\pi_{1,2}$ | λ, Int. | ν | Δν | $m$ | $m\sigma$ |
| 2144·39 (8*R*)<br>2265·04 (8*R*) | 46618·5<br>44135·7 | 2482·8 | (1) | 93607·2<br>96090·0 | —2144·39 (8*R*)<br>—2265·04 (8*R*) | —46618·5<br>—44135·7 | 2482·8 | (1) | 140225·7 |
| *Unclassified Pair of* Cd+. | | | | | 2748·61 (10)<br>2573·0 (10) | 36371·3<br>38853·4 | 2482·1 | (2) | 57236·2 |
| λ | ν | Δν | | | | | | | |
| 2321·13 (8)<br>2194·60 (4) | 43069·3<br>45552·1 | 2482·8 | | | | | | | |

As in the case of zinc, enhanced lines are numerous, more especially in the ultra-violet. The pair of lines 5378·24 (10), 5337·54 (10), wave-numbers 18588·3 and 18730·0, corresponds with the 4924 pair of zinc. The separations of the two pairs are approximately proportional to the squares of the atomic weights.

Observations of the spark spectrum of cadmium in the Schumann region have lately been published by McLennan.*

## MERCURY.

Hg. At. wt.=200·4; At. No.=80.

The wave-lengths for mercury are taken from Cardaun,† Eder and Valenta,‡ Kayser and Runge,‡ Paschen,§ Stiles,|| Wiedmann¶ and Wolff.** The series arrangement is mainly due to Paschen. In addition to the lines given, there are nearly 300 which have not yet been classified. Under certain conditions, mercury yields also a "rich line spectrum," which was first observed by Eder and Valenta.††

A large number of the mercury lines, even the sharp ones, are resolvable, under high dispersion, into several components.‡‡ In general, only the mean wave-lengths are included in the tables.

The limits 1*s* of the principal series of triplets and 2*S* of the singlet series $2S - mP$ have been taken from Wiedmann, and corrected to the International Scale. The other limits have then been calculated from observed lines.

The Hicks formula is found to be inadequate to express the series of mercury except for the higher members. Generally speaking, for values of $m$ lower than 5, the formulæ are not even approximately applicable.

* Proc. Roy. Soc., A. **98**, 106 (1920).
† Zeit. f. Wiss. Phot., **14**, 89 (1915).
‡ Kayser: Handbuch der Spektroscopie, **6**.
§ Ann. d. Phys., **29**, 662 (1909); **30**, 750 (1909); **35**, 869 (1911); Jahrb. d. Rad. u. Elek., **8**, 178.
|| Astrophys. Jour., **30**, 48 (1909).
¶ Ann. d. Phys., **38**, 1041 (1912).
** Ann. d. Phys., **42**, 835 (1913).
†† Denk. Wien Akad., **61**, 401 (1894).
‡‡ Cardaun, loc. cit. Wendt, Dissert. Tubingen, 1911. Janicki, Ann. d. Phys., **39**, (1912). Nagaoka and Takamine, Proc. Phys. Soc., Vol. XV. (1912), &c., &c.

Wiedmann has adopted a more complex grouping for the diffuse triplet series than that given here. Each member of the series, according to his arrangement, consists of one of the tabulated diffuse triplets (excluding the third chief line) together with the corresponding member of the combination series $1p-mD$. He then calls attention to a remarkable relation between this series on the one hand, and an association of the diffuse singlet series with the combination series $1P-md''$, $d'$, on the other. The wave-number differences between corresponding members are found to be constant throughout the series, as shown in the following table for the first two members. With the present classification of the series, however, this relation is a necessary consequence, the constant differences being represented by $1p_{1,\,2,\,3}-1P$.*

| $m$ | Diffuse Singlets and $1P-md''$, $d'$. | | Wave Number Differences. | Diffuse Triplets, as given by Wiedmann. | |
|---|---|---|---|---|---|
| | λ | ν | | ν | λ |
| 2 | 5790·66 | 17264·5 | 10025·7 | 27290·2 | 3663·28 |
| | | | 14656·5 | 31921·0 | 3131·84 |
| | | | 16424·0 | 33688·5 | 2967·52 |
| | 5789·69 | 17267·4 | 10025·8 | 27293·2 | 3662·88 |
| | | | 14656·5 | 31923·9 | 3131·56 |
| | | | 16423·8 | 33691·2 | 2967·28 |
| | 5769·60 | 17327·5 | 10025·8 | 27353·3 | 3654·83 |
| | | | 14656·5 | 31984·0 | 3125·66 |
| | | | — | — | — |
| 3 | 4347·50 | 22995·3 | 10025·9 | 33021·2 | 3027·48 |
| | | | 14656·7 | 37652·0 | 2655·13 |
| | | | — | — | — |
| | 4343·64 | 23015·7 | 10025·9 | 33041·6 | 3025·62 |
| | | | 14656·8 | 37672·5 | 2653·68 |
| | | | 16424·1 | 39439·8 | 2534·77 |
| | 4339·23 | 23039·1 | 10026·0 | 33065·1 | 3023·47 |
| | | | 14656·7 | 37695·8 | 2652·04 |
| | | | — | — | — |

All the measures given in the tables are on the International Scale except those of Wolff in the extreme ultra-violet. The infra-red measures of Paschen have been adjusted in accordance with his correction of their original values.†

* Since the above was written it has been shown by H. Dingle (Proc. Roy. Soc., A. **100**, 167) that it is possible to regard the spectrum as exhibiting a system of quadruplet series, the separations in the subordinate series being respectively 10025·2, 4630·6, 1767·3. The suggested quadruplet system includes all the terms of the tabulated triplet and singlet systems, with the exception of those of the sharp series of singlets.

† Ann. d. Phys., **36**, 197 (1911).

## Hg TRIPLETS.

PRINCIPAL. $1s-mp$. $1s=21830\cdot8$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| —5460·74(10) | —18307·5 | 4630·6 | (1) | 40138·3 |
| —4358·34(10) | —22938·1 | 1767·3 | | 44768·9 |
| —4046·56(10) | —24705·4 | | | 46536·2 |
| 11287·15(10) | 8857·3 | 1545·6 | (2)* | 12973·5 |
| 13673·09(6) | 7311·7 | 145·5 | | 14519·1 |
| 13950·76(2) | 7166·2 | | | 14664·6 |
| 6907·53(10) | 14473·0 | 356·6 | (3) | 7357·8 |
| 7082·01(4) | 14116·4 | 20·2 | | 7714·4 |
| 7092·20(1*r*) | 14096·2 | | | 7734·6 |
| 5803·55(4*r*) | 17226·1 | 164·0 | (4) | 4604·7 |
| †5859·32(4*r*) | 17062·1 | 37·1 | | 4768·7 |
| 5872·12(2) | 17025·0 | | | 4805·8 |
| 5354·05(4*r*) | 18672·4 | 106·3 | (5) | 3158·4 |
| ‡5384·70(3*r*) | 18566·1 | 14·9 | | 3264·7 |
| 5389·01(1) | 18551·2 | | | 3279·6 |
| 5120·65(3*r*) | 19523·4 | 66·2 | (6) | 2307·4 |
| 5138·09(1) | 19457·2 | 7·6 | | 2373·6 |
| 5140·10(1) | 19449·6 | | | 2381·2 |
| 4980·82(3*r*) | 20071·5 | 43·0 | (7) | 1759·3 |
| 4991·5(2) | 20028·5 | — | | 1802·3 |
| —— | —— | | | —— |
| 4890·27(2*r*) | 20443·2 | 27·7 | (8) | 1387·6 |
| 4896·9 (1) | 20415·5 | — | | 1415·3 |
| —— | —— | | | —— |
| 4827·1 (2) | 20710·7 | 21·9 | (9) | 1120·1 |
| 4832·2 (1) | 20688·8 | — | | 1142·0 |
| —— | —— | | | —— |

| $p_1$ | ν | Δν | $m$ | $mp_1$ |
|---|---|---|---|---|
| 4782·1 (1) | 20905·6 | | (10) | 925·2 |
| 4748·1 (1) | 21055·2 | | (11) | 775·6 |
| 4722·8 (1) | 21168·0 | | (12) | 662·8 |
| 4701·8 (1) | 21262·5 | | (13) | 568·3 |
| 4685·3 (1) | 21337·3 | | (14) | 493·5 |
| 4672·7 (1) | 21394·8 | | (15) | 436·0 |
| 4662·4 (1) | 21442·3 | | (16) | 388·5 |
| 4653·4 (1) | 21483·8 | | (17) | 347·0 |

DIFFUSE. $1p-md$. $1p_1=40138\cdot3$ ; $1p_2=44768\cdot9$ ; $1p_3=46536\cdot2$.

| λ, Int. | ν | Δν | $m$ | $md'', d', d$ |
|---|---|---|---|---|
| 3662·88 (4*r*) | 27293·2 | 60·1 | (2) | 12845·1 |
| 3654·83 (6) | 27353·3 | 35·1 | | 12785·0 |
| 3650·15(10) | 27388·4 | | | 12749·9 |
| | | 4630·7 | | |
| 3131·56 (7) | 31923·9 | 60·1 | | |
| 3125·66 (8) | 31984·0 | | | |
| | | 1767·3 | | |
| 2967·28 (5) | 33691·2 | | | |
| 3025·62 (2) | 33041·6 | 23·5 | (3) | 7096·5 |
| 3023·47 (4) | 33065·1 | 21·5 | | 7073·2 |
| 3021·50 (5) | 33086·6 | | | 7051·7 |
| | | 4630·9 | | |
| 2653·68 (4) | 37672·5 | 23·3 | | |
| 2652·04 (5) | 37695·8 | | | |
| | | 1767·3 | | |
| 2534·77 (4) | 39439·8 | | | |
| 2805·42 (1) | 35635·0 | 12·1 | (4) | 4502·7 |
| 2804·46 (2) | 35647·1 | 12·5 | | 4491·0 |
| 2803·48 (4) | 35659·6 | | | 4478·7 |
| | | 4631·6 | | |
| 2482·72 (3) | 40266·6 | 11·5 | | |
| 2482·01 (4) | 40278·1 | | | |
| | | 1767·2 | | |
| 2378·34 (3) | 42033·8 | | | |
| —— | —— | | (5) | 3110·2 |
| 2699·50 (1*n*) | 37033·1 | 8·9 | | 3104·5 |
| 2698·85 (3*n*) | 37042·0 | | | 3096·3 |
| | | 4632·1 | | |
| 2399·74 (2) | 41658·9 | 6·3 | | |
| 2399·38 (3) | 41665·2 | | | |
| | | 1767·0 | | |
| 2202·09 (2*n*) | 43425·9 | | | |
| 2639·93 (3*n*) | 37868·8 | | (6) | 2279·4 |
| 2352·48 (1*n*) | 42495·8 | | | 2273·1 |
| 2258·87 (1) | 44256·8 | | | 2269·5 |
| 2603·15 (2*n*) | 38403·8 | | (7) | —— |
| 2323·30 (1*n*) | 43029·5 | | | 1739·4 |
| —— | —— | | | 1734·5 |

* Paschen hesitates between this triplet and (12390·7), 13950·76, (?), the latter being indicated by a formula. The line $1S-2p_2$, however, afterwards discovered by Wolff, indicates that the above triplet is the true one.

† Has satellites λ5860·10 and λ5868·08.

‡ Has satellite λ5385·79.

## Hg Triplets—*Continued.*

Sharp. $1p$—$ms$.
)138·3 ; $1p_2$=44768·9 ; $1p_3$=46536·2.

| | ν | Δν | m | ms |
|---|---|---|---|---|
| .0) | 18307·5 | 4630·6 | (1) | 21830·8 |
| .0) | 22938·1 | 1767·3 | | |
| 10) | 24705·4 | | | |
| (6) | 29918·3 | 4630·8 | (2) | 10219·9 |
| (5) | 34549·1 | 1767·3 | | |
| (4) | 36316·4 | | | |
| (4) | 34173·4 | 4630·8 | (3) | 5964·7 |
| (3) | 38804·2 | 1767·4 | | |
| (2) | 40571·6 | | | |
| (3) | 36225·3 | 4630·8 | (4) | 3912·8 |
| (2) | 40856·1 | 1767·4 | | |
| (1) | 42623·5 | | | |
| (2) | 37372·5 | 4632·1 | (5) | 2765·0 |
| (1) | 42004·6 | — | | |
| - | — | | | |
| (2) | 38080·7 | 4630·8 | (6) | 2057·5 |
| (1) | 42711·5 | — | | |
| - | — | | | |
| (1) | 38548·0 | | (7) | 1590·3 |
| - | — | | | — |
| - | — | | | — |

ed by Paschen to be a double line with on=10 A.U.

Fundamental. $2d$—$mf$.
$2d$=12749·9 ; $2d'$=12785·0 ; $2d''$=12845·1.

| λ, Int. | ν | m | mf |
|---|---|---|---|
| 17193 (1) | 5814·8 | (3) | 6939·9 |
| 17108·5 (1) | 5843·5 | | |
| 16938·9 (2) | 5902·0 | | |
| 12020·2 (1) | 8317·2 | (4) | 4433·6 |
| — | — | | |
| *11886·6 (1) | 8410·6 | | |

Combination. $1p$—$mf$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 3011·05 (1$n$) | 33201·4 | $1p_1$—$3f$=33198·4 |
| 2462·60 (1) | 37830·5 | $1p_2$—$3f$=37829·0 |
| 2524·71 (1$r$) | 39596·9 | $1p_3$—$3f$=39596·3 |
| 2799·83 (2) | 35706·1 | $1p_1$—$4f$=35704·7 |
| 2478·1 (1) | 40342·1 | $1p_2$—$4f$=40335·3 |
| 2374·02 (2$n$) | 42110·2 | $1p_3$—$4f$=42102·6 |

Other Combinations.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 3680·01 (5) | 27166·1 | $1p_1$—$2p_1$=27164·8 |
| 3050·46 (1$n$) | 32772·5 | $1p_1$—$3p_1$=32780·5 |
| 3085·29 (1$n$) | 32402·5 | $1p_1$—$3p_3$=32403·7 |
| 3144·48 (2$r$) | 31792·6 | $1p_2$—$2p_1$=31795·4 |
| 3305·09 (1$r$) | 30247·7 | $1p_2$—$2p_2$=30249·8 |
| 2672·67 (1$n$) | 37404·9 | $1p_2$—$3p_1$=37411·1 |
| 3135·76 (2$n$) | 31881·0 | $1p_3$—$2p_3$=31871·6 |
| 36258 (2) | 2757·3 | $2p_1$—$2s$ = 2753·6 |
| 23263 (3) | 4297·6 | $2p_2$—$2s$ = 4299·2 |
| 22489 (3) | 4445·4 | $2p_3$—$2s$ = 4444·7 |

## Hg Singlets.

Principal. $1S$—$mP$.
$1S$=84178·5.

| | ν | m | mP |
|---|---|---|---|
| )·57 | 54065·7 | (1) | 30112·8 |
| 2·72 | 71290·6 | (2) | 12887·9 |

Diffuse. $1P$—$mD$.
$1P$=30112·8.

| nt. | ν | m | mD |
|---|---|---|---|
| 6 (10$r$) | 17264·5 | (2) | 12848·3 |
| 0 (6$n$) | 22995·3 | (3) | 7117·5 |
| 0 (4$n$) | 25591·8 | (4) | 4521·0 |
| 2 (1) | 26988·6 | (5) | 3124·2 |
| 7 (1) | 27824·4 | (6) | 2288·4 |
| 7 (2) | 28366·7 | (7) | 1746·1 |
| 8 (1) | 28736·4 | (8) | 1376·4 |
| 2 (1) | 29001·0 | (9) | 1111·8 |

Sharp. $1P$—$mS$.
$1P$=30112·8.

| λ, Int. | ν | m | mS |
|---|---|---|---|
| —1849·57 | —54065·7 | (1) | 84178·5 |
| 10139·67 (24) | 9859·7 | (2) | 20253·1 |
| 4916·04 (4$r$) | 20335·9 | (3) | 9776·9 |
| 4108·08 (2$n$) | 24335·4 | (4) | 5777·4 |
| 3801·67 (2) | 26296·8 | (5) | 3816·0 |

* λ vac., Wolff.

† Paschen obtains this line by assuming λ13570·68 as the value of $2S$—$2P$. He questions the truth of this, however, and the value of $2P$ which it gives leads to a line for $1s$—$2P$ which has not been observed, and which is unexpectedly close to $1s$—$2p_1$. It is probable, therefore, that λ1402·72 and λ13570·68 do not take part in the above series, but are combination lines, associated by the fact that their wave-number difference is equal to $1S$—$2S$.

## Hg SINGLETS—*Continued.*

FUNDAMENTAL. $2D—mF$.
$2D=12848·3$.

| λ, Int. | ν | $m$ | $mF$ |
|---|---|---|---|
| 16918·3 (2) | 5909·2 | (3) | 6939·1 |
| *11886·6 (1) | 8410·6 | (4) | 4437·7 |

COMBINATION. $1P—mF$.
$1P=30112·8$.

| λ | ν | ν calc. |
|---|---|---|
| 4313·3 (1 $v$) | 23177·7 | $1P—3F=23173·7$ |
| 3893·89 (1$n$) | 25674·2 | $1P—4F=25675·1$ |

* Stated by Paschen to be a double line with separation=10 A.U.
† Used in calculation of Principal series.

COMBINATION. $2S—mP$.
$2S=20253·1$.

| λ, Int. | ν | $m$ | $mP$† |
|---|---|---|---|
| —10139·67 (24) | —9859·7 | (1) | 30112·8 |
| 13570·68 (?)(4) | 7366·9 (?) | (2) | 12886·2 (?) |
| 6716·45 (?)(5) | 14884·8 (?) | (3) | 5368·3 (?) |
| 6234·35 (8) | 16035·8 | (4) | 4217·3 |
| ‡5803·55 (4$r$) | 17226·1 | (5) | 3027·0 |
| 5549·28 (3$r$) | 18015·4 | (6) | 2237·7 |
| 5393·50 (2) | 18535·8 | (7) | 1717·3 |
| 5290·1 (2) | 18897·9 | (8) | 1355·2 |
| 5218·9 (2) | 19155·7 | (9) | 1097·4 |
| 5165·8 (1) | 19352·2 | (10) | 900·9 |
| 5128·9 (1) | 19492·0 | (11) | 761·1 |

‡ This line occurs also as $1s—4p_1$. It is very diffuse, and is considered by Paschen to arise from both sources.

## Hg INTER-COMBINATIONS.

COMBINATION. $1p—mD$.
$1p_1=40138·3$; $1p_2=44768·9$; $1p_3=46536·2$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 3663·28 (5) | 27290·2 | $1p_1—2D=27290·0$ |
| 3131·84 (7) | 31921·0 | $1p_2—2D=31920·6$ |
| 2967·52 (1) | 33688·5 | $1p_3—2D=33687·9$ |
| 3027·48 (2) | 33021·2 | $1p_1—3D=33020·8$ |
| 2655·13 (4) | 37652·0 | $1p_2—3D=37651·4$ |
| ——* | —— | $1p_3—3D=39418·7$ |
| 2806·84 (1) | 35616·9 | $1p_1—4D=35617·3$ |
| 2483·83 (2) | 40248·6 | $1p_2—4D=40247·9$ |
| 2379·46 | 42013·8 | $1p_3—4D=42015·2$ |
| 2700·92 (1) | 37013·7 | $1p_1—5D=37014·1$ |
| 2400·52 (0) | 41645·4 | $1p_2—5D=41644·7$ |
| —— | —— | $1p_3—5D=43412·0$ |

COMBINATION. $1p_2—mS$.

| λ | ν | ν calc. |
|---|---|---|
| —2536·52 (10$n$) | —39412·6 | $1p_2—1S=$ —39409·6 |
| 4077·83 (7$r$) | 24515·9 | $1p_2—2S=$ 24515·8 |
| 2856·94 (1) | 34992·4 | $1p_2—3S=$ 34992·0 |
| 2563·90 (1) | 38991·7 | $1p_2—4S=$ 38991·5 |

* Probably hidden by strong diffuse line λ2536·52 (ν=39412·6).

COMBINATION. $1P—md$.
$1P=30112·8$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 5789·69 (2) | 17267·4 | $1P—2d''=$ 17267·7 |
| 5769·60 (10$r$) | 17327·5 | $1P—2d'=$ 17327·8 |
| —— | —— | |
| 4343·64 (2) | 23015·7 | $1P—3d''=$ 23016·3 |
| 4339·23 (4) | 23039·1 | $1P—3d'=$ 23039·6 |
| —— | —— | |
| 3903·64 (2) | 25609·9 | $1P—4d''=$ 25610·1 |
| 3901·90 (2$n$) | 25621·3 | $1P—4d'=$ 25621·8 |
| —— | —— | |
| 3702·36 (1) | 27002·3 | $1P—5d''=$ 27002·6 |
| 3701·44 (1) | 27008·8 | $1P—5d'=$ 27008·3 |
| —— | —— | |
| 3591·48 (1) | 27835·9 | $1P—6d''=$ 27833·4 |
| 3590·95 (1) | 27840·0 | $1P—6d'=$ 27839·7 |
| —— | —— | |
| —— | —— | |
| 3523·00 (1) | 28377·2 | $1P—7d'=$ 28373·4 |
| —— | —— | |
| —— | —— | |
| 3477·85 (1) | 28745·5 | $1P—8d'=$ |
| —— | —— | |

Hg INTER-COMBINATIONS—*Continued.*

| COMBINATION. $1S—mp_2$. | | |
|---|---|---|
| λ, Int. | ν | ν calc. |
| 2536·52 (10*n*) | 39412·6 | $1S—1p_2=39409·6$ |
| *1435·63 | 69655·8 | $1S—2p_2=69659·4$ |

| COMBINATION. $1P—ms$. | | |
|---|---|---|
| λ | ν | ν calc. |
| 12070·23 (1) | 8282·7 | $1P—1s=8282·0$ |
| 5025·56 (3) | 19892·8 | $1P—2s=19892·9$ |
| 4140·03 (1) | 24147·9 | $1P—3s=24148·1$ |
| 3815·84 (1) | 26199·3 | $1P—4s=26200·0$ |

* λ vac., Wolff.

| COMBINATION LINE. | | |
|---|---|---|
| λ, Int. | ν | ν calc. |
| 17071·54 (2) | 5856·2 | $2p_1—3D=5856·0$ |

| COMBINATION. $1s—mP$. | | |
|---|---|---|
| λ | ν | ν calc. |
| —12070·23 (1) | —8282·7 | $1s—1P=-8282·0$ |
| ? | ? | |
| 6072·63 (5) | 16462·9 | $1s—3P=16462·5$ |
| 5675·86 (5) | 17614·5 | $1s—4P=17613·5$ |
| 5316·69 (3*v*) | 18803·6 | $1s—5P=18803·8$ |
| 5102·42 (2*v*) | 19593·1 | $1s—6P=19593·1$ |
| 4970·13 (1*v*) | 20114·7 | $1s—7P=20113·5$ |
| 4883·1 (1) | 20474·6 | $1s—8P=20475·6$ |
| 4822·3 (1) | 20731·3 | $1s—9P=20733·4$ |

## IONISED MERCURY ($Hg^+$).

The enhanced lines of mercury do not appear to have been investigated in relation to possible series. Rydberg, however, noted a pair of lines in the ultra-violet which appeared to be analogous with the pairs of ionised zinc and cadmium which have already been mentioned. The wave-lengths of these lines as given by Cardaun are shown below, together with the wave-numbers and separation.

| λ, Int. | ν | Δν |
|---|---|---|
| 2847·83 (8*n*) | 35104·16 | 9829·3 |
| 2224·82 (3*n*) | 44933·44 | |

These lines have been found to give Zeeman resolutions of the type of $D_2$ and $D_1$ of sodium, and possibly represent a principal pair. They are among the enhanced lines identified as such by Steinhausen.

For the pairs of Zn, Cd, Hg, the values of Δν divided by the squares of the atomic weights are respectively ·204, ·197, ·246.

# CHAPTER XVI.

## GROUP IIIA.—SCANDIUM, YTTRIUM, AND RARE EARTHS.

Series in the elements of this sub-group have not yet been clearly identified. From analogy with previous groups it would be expected that the *arc* spectra would resemble the elements of Group IIIB., and give series of doublets. The *spark* spectra, on the other hand, might show triplets. The difficulty of analysing the spectra is increased by the fact that the (enhanced) lines of the ionised elements are well developed even by the stimulus of the electric arc, and that the two spectra have only been partially separated in most cases.

Hicks has stated* that he has found evidence of doublet series of $S$ and $D$ types in Sc, Y, La and Yb, but details have only been given for Sc. A tentative arrangement of the possible two series of this element† suggested the limits $1\pi_1=37950$ for the sharp series, and $1\sigma=22282$ for the principal series, with the doublet separation $\Delta\nu=320{\cdot}8$.

The question of constant differences in some of these spectra has been investigated by Paulson, but the details are too extensive for quotation.

Probably the most important contribution to the analysis of the spectra is that of Popow,‡ who based his results on observations of the effects of a magnetic field which were made in Paschen's laboratory at Tübingen.

Popow did not succeed in identifying any complete series, but only some combination groups, which will be best understood by reference to the corresponding combinations of calcium or strontium. The combinations in question are those indicated by $1d-2p$. Being connected with a triplet system, each term has three values, but of the nine possible combinations only six appear. In the form adopted by Popow, the strontium group, with our notation and numeration, would be represented thus :—

| | | | | | |
|---|---|---|---|---|---|
| | | | | 15668 | $2p_3$ |
| | | | | 41 | |
| | | 15649 | 60 | 15709 | $2p_2$ |
| | | 105 | | 105 | |
| 15654 | 100 | 15754 | 60 | 15814 | $2p_1$ |
| $1d$ | | $1d'$ | | $1d''$ | |

The $p$ and $d$ terms may here be regarded as co-ordinates, and 15649, for instance, is to be read as $1d'-2p_2$. The differences $1d'-1d$, $1d''-1d'$ give the separations of the fundamental series ; $2p_1-2p_2$, $2p_2-2p_3$ give the separations in the second member of the principal series.

*Scandium* (Sc. At. wt.=44·1 ; At. No.=21).—A combination group of this type, according to Popow, is composed of the lines :—

| $\lambda$ (Rowd.) | $\nu$ |
|---|---|
| 2563·30 (2) | 39000·8 |
| 60·35 (3) | 045·6 |
| 55·90 (2) | 113·7 |
| 52·46 (3) | 166·2 |
| 45·24 (2) | 276·99 |
| 40·94 (1) | 344·05 |

* Phil. Trans., A. **212**, 34 (1913).
† Hicks, Phil. Trans., A. **213**, 409 (1914).
‡ Ann. d. Phys., **45**, 163 (1914).

The suggested arrangement is as follows :—

| | | | | | |
|---|---|---|---|---|---|
| | | | | 39000·80 | $p_3$ |
| | | | | 112·88 | |
| | | 39045·57 | 68·11 | 39113·68 | $p_2$ |
| | | 231·42 | | 230·37 | |
| 39166·23 | 110·76 | 39276·99 | 67·06 | 39344·05 | $p_1$ |
| $d$ | | $d'$ | | $d''$ | |

In terms of the Ritz equation, Popow designates the group as $3d^i-3p^j$, which becomes $1(?2)d-2p$ in the notation of the present report.

It is of importance to note that, according to the tables of Exner and Haschek, the lines in question are probably of the enhanced type.

*Yttrium* (Y. At. wt.=88·8; At. No.=39).—Two groups are given by Popow for Yttrium, designated respectively $3d^i-2p^j$ and $3d^i-3p^j$. The wave-numbers are

| | | | | | |
|---|---|---|---|---|---|
| | | | | 22604·07 | $1p_3$ |
| | | | | 331·20 | |
| | | 22730·31 | 204·96 | 22935·27 | $1p_2$ |
| | | 871·22 | | 870·90 | |
| 23196·67 | 404·86 | 23601·53 | 204·64 | 23806·17 | $1p_1$ |
| $2d$ | | $2d'$ | | $2d''$ | |
| | | | | 31207·57 | $2p_3$ |
| | | | | 75·27 | |
| | | 31077·98 | 204·86 | 31282·84 | $2p_2$ |
| | | 159·47 | | 159·46 | |
| 30832·61 | 404·84 | 31237·45 | 204·85 | 31442·30 | $2p_1$ |
| $2d$ | | $2d'$ | | $2d''$ | |

It may be deduced that the separations of the narrow triplets of the fundamental series are probably 405 and 205, while those of the first member of the principal series, and therefore the main separations in the subordinate series, would be 870 and 331.

Lines of the first group are included among the enhanced lines given by Lockyer; those of the second group were not within the range of his investigation, and the observations of Exner and Haschek merely indicate that with one exception the lines are strong in both arc and spark.

*Lanthanum* (La. At. wt.=139·0; At. No.=57).—The following group for lanthanum is given by Popow as the combination $3d^i-3p^j$ :—

| | | | | | |
|---|---|---|---|---|---|
| | | | | 29889·59 | $2p_3$ |
| | | | | 375·19 | |
| | | 29568·35 | 696·43 | 30264·78 | $2p_2$ |
| | | 1043·44 | | 1043·63 | |
| 29953·03 | 658·76 | 30611·79 | 696·62 | 31308·41 | $2p_1$ |
| $2d$ | | $2d'$ | | $2d''$ | |

The separation $\Delta d$ (=658·76) is here smaller than $\delta d$ (=696·6), whereas in the other elements considered it is greater. An irregularity in the arrangement of the

satellites in the related diffuse triplets is therefore suggested, if the combinations have been correctly identified.

The available evidence does not very strongly point to the above lines being of the enhanced type, but Exner and Haschek's observations suggest that two of the lines are enhanced. In the visible spectrum the only enhanced lines tabulated as such by Lockyer are $\lambda$4192·5 and 4099·7.

From the data for Sc and Y, Popow deduces the formulæ—

$$0{\cdot}529 \log \Delta p = \log A - 0{\cdot}395$$
$$0{\cdot}652 \log \delta p = \log A - 0{\cdot}305$$

where $A$ = At. wt.; $\Delta p = p_2 - p_1$; $\delta p = p_3 - p_2$

He then calculates that for Al, $\Delta p = 92$, $\delta p = 53{\cdot}5$, which do not compare favourably with the separations of the probable triplet, 128, 64. It may be observed, however, that in the atomic weight relation Al belongs to the Ga, In, Tl sub-group, and agreement need not be expected with the elements of the first sub-group. At all events, in the first and second groups the sub-groups do not show a common atomic weight relation.

The general result of the discussion of the three elements is to suggest that the enhanced lines probably form triplet series.

Of the "rare earths" having atomic numbers ranging from 57 to 71, many have been examined by Paulson* for "constant differences." Numerous lines of this class have been found, but it is scarcely possible to give any useful summary of the results. Europium, however, is possibly of special interest, as in some arrangements of the periodic table it is suggested that this element should fall in Group II., between Cd and Hg. Paulson finds four pairs of strong lines with separation 1669·7, and twelve weaker pairs with the same separation. Hicks,† on the other hand, considers that the spectrum consists of triplets, having separations 2631 and 1004, the limit of the sharp series ($s_1\infty$) being 40364. The diffuse series suggested by Hicks, however, is very imperfect, and the question cannot be considered settled one way or the other.

As bearing on the place of gadolinium in the periodic table, Hicks thinks it probable that this element falls in Group IIIB., between indium and thallium, on the ground that there is a large number of doublets of separation about 5000. No details are given, and this separation does not appear among those noted by Paulson.

There are no data relating to the spectrum of actinium.

* Astrophys. Jour., **40**, 298 (1914). *See also* p. 26.
† Phil. Trans., A. **212**, 59 (1913).

# CHAPTER XVII.

## GROUP IIIB.—THE ALUMINIUM SUB-GROUP.

The arc spectra of the elements Al, Ga, In, and Tl, forming a sub-group of Group III. of the periodic table, present series of doublets. The subordinate series were early identified by Rydberg and by Kayser and Runge, and the principal series were afterwards found by Paschen. The series have a general resemblance to those of the alkali metals, but the separations are greater as compared with the increase of atomic weights. Also, in these spectra the first principal pair occurs with negative sign, and the other members of the principal series lie on the red side of the sub-ordinate series, whereas in the alkali metals the principal series lie on the more refrangible side of the sharp and diffuse series. As in the case of the alkali metals, there are very few lines which have not been placed in one or other of the four main series, or are to be accounted for as combinations.

The spectrum of boron probably lies mainly in the region of short wave-lengths, and complete series have not yet been traced.

Little progress has been made in the detection of regularity in the spark spectra of these elements.

### BORON.

B. At. wt.=11·0; At. No.=5.

The arc spectrum of boron in the region ordinarily observed is of remarkable simplicity, consisting of a close pair of lines in the ultra-violet, for which wave-lengths have been given by several observers. The values from Rowland's measures are:—

| $\lambda$ | $\nu$ | $\Delta\nu$ |
|---|---|---|
| 2497·73 (10*R*) | 40024·3 | |
| 96·78 (8*R*) | 039·6 | 15·3 |

Rydberg was probably right in supposing this to be the first pair of the sharp and principal series, but the formulæ which he suggested for the series depended upon the use of spark lines, and are probably therefore of no significance.

Dr. M. A. Catalán * has recently drawn attention to a second pair of arc lines, observed by Sr. Piña de Rubies, which have a separation practically identical with that of the original pair, namely—

| $\lambda$ | $\nu$ | $\Delta\nu$ |
|---|---|---|
| 2089·49 | 47843·2 | |
| 88·84 | 58·1 | 14·9 |

An extension of the observations into the region of shorter wave-lengths would seem to be necessary for the calculation of formulæ, but meanwhile the observations are of interest as indicating the separation in the doublets constituting the series.

As many as seventeen lines were observed in the spark spectrum by Eder and Valenta, but, with specially pure material, only three lines were found by Crookes,† two of which form the pair at $\lambda$2497, while the third has the wave-length 3451·35.

* An. Soc. Española Fis. y Quim., 15, No. 38 (1917).
† Proc. Roy. Soc., A. 86, 36 (1911).

## Al DOUBLETS.

PRINCIPAL. $1\sigma - m\pi$.
$1\sigma = 22933{\cdot}27$.

| λ, Int. | ν | Δν | m | $m\pi_{1,2}$ |
|---|---|---|---|---|
| —3961·540(10*R*) | —25235·60 | 112·01 | (1) | 48168·87 |
| —3944·032(10*R*) | — 347·61 | | | 280·88 |
| 13125·36 | 7616·79 | 15·22 | (2) | 15316·48 |
| 13151·65 | 01·57 | | | 331·70 |
| 6696·064 (3) | 14930·03 | 5·95 | (3) | 8003·24 |
| 98·734 (3) | 924·08 | | | 09·19 |
| 5557·08 (1*n*) | 17990·08 | 2·82 | (4) | 4943·19 |
| 57·95 (1*n*) | 987·26 | | | 46·01 |
| *5105·14 | 19582·7 | 2·0 | (5) | 3350·6 |
| * 05·64 | 580·7 | | | 52·6 |

SHARP. $1\pi - m\sigma$.
$1\pi_1 = 48168{\cdot}84$ ; $1\pi_2 = 48280{\cdot}91$.

| λ, Int. | ν | Δν | m | $m\sigma$ |
|---|---|---|---|---|
| 3961·540(10*R*) | 25235·60 | 112·01 | (1) | 22933·27 |
| 44·032(10*R*) | 347·61 | | | |
| 2660·393(10*R*) | 37577·28 | 112·03 | (2) | 10591·58 |
| 52·484(10*R*) | 689·31 | | | |
| 2378·408 (3) | 42032·08 | 112·06 | (3) | 6136·76 |
| 72·084 (3) | 144·14 | | | |
| 2263·731 (2) | 44161·16 | 112·09 | (4) | 4007·67 |
| 57·999 (2) | 273·25 | | | |
| *†2204·66 (4) | 45344·3 | | (5) | 2833·2 |
| 2199·64 (1) | 447·7 | | | |

Al COMBINATIONS.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 21166·3 | 4723·23 | $2\pi_1 - 2\sigma = 4724{\cdot}90$ |
| 21098·2 | 4738·47 | $2\pi_2 - 2\sigma = 4740{\cdot}12$ |
| 16752·2 | 5967·76 | $2\pi_1 - 3\delta = 5969{\cdot}26$ |
| 16720·5 | 5979·07 | $2\pi_2 - 3\delta' = 5979{\cdot}99$ |
| * 2426·14(4*r*) | 41205·2 | $1\pi_1 - 3\varphi = 41206{\cdot}3$ |
| * 19·56(2*r*) | 317·2 | $1\pi_2 - 3\varphi = 41318{\cdot}3$ |
| * 2312·48(2) | 43230·4 | $1\pi_1 - 4\pi_1 = 43225{\cdot}7$ |
| * 2231·20(1*r*) | 44804·9 | $1\pi_1 - 5\pi_1 = 44818{\cdot}3$ |
| * 25·70(1*r*) | 915·7 | $1\pi_2 - 5\pi_2 = 44928{\cdot}3$ |

* Kayser and Runge (other lines by Paschen or Grünter).
† Confused with a δ line.
‡ This and three following lines are given as arc lines by K.R., but Huppers records them only in the spark.
§ Satellites not seen beyond this.

DIFFUSE. $1\pi - m\delta$.
$1\pi_1 = 48168{\cdot}84$ ; $1\pi_2 = 48280{\cdot}91$.

| λ, Int. | ν | Δν | m | $m\delta'$, δ |
|---|---|---|---|---|
| 3092·843(6*R*) | 32323·36 | 1·33 | (2) | 15845·49 |
| 92·716(10*R*) | 324·69 | | | 844·15 |
| | | 112·04 | | |
| 3082·159(10*R*) | 32435·40 | | | |
| 2575·411(3*R*) | 38817·13 | 4·49 | (3) | 9351·71 |
| 75·113(10*R*) | 821·62 | | | 47·22 |
| | | 112·07 | | |
| 2567·997(10*R*) | 38929·20 | | | |
| 2373·360(2*R*) | 42121·49 | 4·04 | (4) | 6047·37 |
| 73·132(8*R*) | 125·53 | | | 43·31 |
| | | 112·03 | | |
| 2367·064(8*R*) | 42233·52 | | | |
| §2269·212(2*R*) | 44054·51 | 2·31 | (5) | 4114·33 |
| 69·093(4*R*) | 056·82 | | | 12·09 |
| | | 112·07 | | |
| 2263·453(4*R*) | 44166·58 | | | |
| 2210·046(2*R*) | 45233·78 | | (6) | 2935·96 |
| 04·627(2*R*) | 344·95 | | | 35·06 |
| 2174·028(1*R*) | 45983·10 | | (7) | 2187·09 |
| 68·805(1*R*) | 46093·82 | | | 85·74 |
| 2150·59 (1) | 46484·2 | | (8) | 1684·3 |
| 45·39 (1) | 596·9 | | | |
| 2134·70 (1) | 46830·2 | | (9) | 1336·9 |
| 29·44 (1) | 945·8 | | | |
| *2123·38 (1) | 47079·9 | | (10) | 1091·0 |
| * 18·52 (1) | 187·8 | | | |

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 15844{\cdot}8$.

| λ | ν | Δν | m | $m\varphi$ |
|---|---|---|---|---|
| 11255·5 | 8882·2 | | (3) | 6962·6 |
| 8774·7 | 11393·3 | | (4) | 4451·5 |

*Unclassified Lines of* Al.

| λ, Int. | ν | λ | ν |
|---|---|---|---|
| 3066·16 (4) | 32604·6 | 2321·57 (2) | 43060·7 |
| 64·30 (4) | 624·4 | ‡19·05 (2) | 107·9 |
| 59·93 (2) | 671·0 | 17·48 (2) | 137·1 |
| 57·16 (5) | 700·6 | 14·98 (2) | 183·7 |
| 54·70 (4) | 726·9 | 13·53 (2) | 210·7 |
| 50·08 (4) | 776·6 | | |

## ALUMINIUM.

Al. At. wt.=27·1 ; At. No.=13.

An excellent series of measures of the lines constituting the arc spectrum of aluminium was made by Kayser and Runge, and it is still necessary to make use of their determinations of some of the fainter lines. Wave-lengths of arc and spark lines on the new scale have been determined over a long range (6929-2129) by R. Grünter,* and in the region more refrangible than λ3200 by W. Huppers.† Measures in the region 2500-1850 have also been given for the spark by Eder.‡

The vacuum arc spectrum in the Schumann region has been observed by McLennan,§ but no connection of the lines with the established series has been recognised. It should be observed that the vacuum arc usually develops spark lines, so that the true arc lines in this region, if any, are not known.

Reference has already been made (p. 39) to the abnormal arrangement of the satellites, and to the difficulty of representing the diffuse series by a simple formula.

The adopted limits are based upon those calculated by Dunz for the sharp series.

### IONISED ALUMINIUM ($Al^+$).

Enhanced lines of aluminium are numerous and well marked, but no series have yet been traced. The most recent measures are those of Grünter, which extend from the red to the ultra-violet. The spark lines in the Schumann region have been tabulated, and a photograph reproduced, by Lyman.‖

In connection with Kossel and Sommerfeld's "displacement law" (p. 74), according to which the ionised elements of the Al sub-group should exhibit triplet series, it should be noted that Popow¶ had previously directed attention to the following triplets, which may represent $Al^+$ :—

| λ vac. | ν | Δν |
|---|---|---|
| 1765·7 (8) | 56635 | |
| 61·9 (8) | 757 | 122 |
| 60·0 (8) | 818 | 61 |
| 1725·0 (10) | 57971 | |
| 21·2 (9) | 58099 | 128 |
| 19·3 (9) | 163 | 64 |

The second triplet is quite isolated, but the first occurs as part of a group of five lines, and some doubt is thrown upon its assignment to $Al^+$ by the fact that McLennan did not observe the third line in the vacuum arc.

## GALLIUM.

Ga. At. wt.=69·9 ; At. No.=31.

Very few lines have been observed in the spectrum of gallium, but it is possible that the records are incomplete in consequence of difficulty in obtaining material for experiment. While the spectrum was almost unknown, Rydberg made an

* Zeit. f. Wiss. Phot., **13**, 1 (1914).
† *Ibid.*, **13**, 46.
‡ *Ibid.*, **13**, 20 ; **14**, 137 (1915).
§ Proc. Roy. Soc., A. **95**, 323 (1919).
‖ "Spectroscopy of the Extreme Ultra-Violet."
¶ Ann. d. Phys., **45**, 166 (1914).

interesting calculation of the formulæ for the subordinate series by interpolation from the constants for related elements. For the limits of the subordinate series he deduced 47390 and 48222, and the calculated positions of some of the lines were not very widely different from those subsequently observed. Our knowledge of the series has been extended by Paschen and Meissner,* whose observations have been utilised in the table which follows. All the known arc lines are included in the table.

Exner and Haschek have recorded nine lines which are special to the spark spectrum in the region λ4172 to λ2450, and other spark lines were recorded in the visible spectrum by the discoverer of gallium, Lecoq de Boisbaudran.†

Ga DOUBLETS.

PRINCIPAL. $1\sigma - m\pi$. $1\sigma = 23591{\cdot}5$.

| λ, Int. | ν | Δν | $m$ | $m\pi_{1,2}$ |
|---|---|---|---|---|
| —4172·06 (30*R*) | —23962·3 | 826·0 | (1) | 47553·8 |
| —4033·03 (30*R*) | —24788·3 | | | 48379·8 |
| *[11940] | [8373] | | (2) | [15218] |
| *[12096] | [8265] | | | [15326] |
| 6396·89 | 15628·3 | 41·1 | (3) | 7963·2 |
| 6413·77 | 587·2 | | | 8004·3 |
| 5353·81 | 18673·1 | 20·9 | (4) | 4918·4 |
| 59·8 | 652·2 | | | 39·3 |

DIFFUSE. $1\pi - m\delta$. $1\pi_1 = 47553{\cdot}8$; $1\pi_2 = 48379{\cdot}8$.

| λ, Int. | ν | Δν | $m$ | $m\delta'$, δ |
|---|---|---|---|---|
| 2944·18 (5*R*) | 33955·4 | 6·0 | (2) | 13598·3 |
| 43·66 (10*R*) | 961·4 | | | 592·4 |
| | | 826·2 | | |
| 2874·24 (10*R*) | 34781·6 | | | |
| —— | —— | | (3) | 7577·1 |
| 2500·18 (2*R*) | 39985·1 | | | 68·7 |
| 2450·10 (2*R*) | 40802·7 | | | |

SHARP. $1\pi - m\sigma$. $1\pi_1 = 47553{\cdot}8$; $1\pi_2 = 48379{\cdot}8$.

| λ, Int. | ν | Δν | $m$ | $m\sigma$ |
|---|---|---|---|---|
| 4172·06 (30) | 23962·3 | 826·0 | (1) | 23591·5 |
| 4033·03 (30) | 24788·3 | | | |
| 2719·66 (3) | 36758·5 | 826·6 | (2) | 10795·0 |
| 2659·84 (2) | 37585·1 | | | |

COMBINATION.

| λ | ν | ν *calc.* |
|---|---|---|
| 3020·49 (3) | 33097·6 | $1\pi_2 - 2\pi_2 = 33054$ |

* Calculated lines.

INDIUM.

In. At. wt.=114·8; At. No.=49.

The sharp and diffuse series of indium doublets were identified by Kayser and Runge, and by Rydberg, and the principal series by Paschen and Meissner.‡ The limits adopted for the subordinate series are those determined from the sharp series by Johanson. These lead to a limit for the principal series which is almost identical with that calculated independently by Paschen and Meissner (22294·9). As in aluminium, the satellite in the first diffuse pair is abnormally close to the chief line.

The wave-lengths, other than for the principal series, are due to Kayser and Runge. The infra-red region has not been observed, and the fundamental series

* Ann. d. Phys., **43**, 1223 (1914).
† Comptes Rendus, **82**, 168 (1876).
‡ Ann. d. Phys., **43**, 1223 (1914).

## In Doublets.

**Principal.** $1\sigma - m\pi$. $1\sigma = 22294{\cdot}8$.

| λ, Int. | ν | Δν | $m$ | $m\pi_{1,2}$ |
|---|---|---|---|---|
| —4511·27 (10*R*) | —22160·5 | 2212·6 | (1) | 44455·3 |
| —4101·72 (8*R*) | —24373·1 | | | 46667·9 |
| | | | (2) | [14519] |
| | | | | [14811] |
| 6847·77 (8) | 14599·3 | 111·3 | (3) | 7695·5 |
| 6900·37 (6) | 488·0 | | | 7806·8 |
| 5209·75 (5) | 17509·1 | 56·6 | (4) | 4785·7 |
| 28·27 (4) | 452·5 | | | 4842·3 |
| 5253·97 (3) | 19027·9 | 30·4 | (5) | 3266·9 |
| 62·38 (2) | 18997·5 | | | 97·3 |
| 5017·5 (1) | 19924·7 | 21·8 | (6) | 2370·1 |
| 23·0 (0) | 902·9 | | | 91·9 |
| 4878·8 (0) | 20491·1 | | (7) | 1803·7 |

**Sharp.** $1\pi - m\sigma$. $1\pi_1 = 44455{\cdot}3$ ; $1\pi_2 = 46667{\cdot}9$.

| λ, Int. | ν | Δν | $m$ | $m\sigma$ |
|---|---|---|---|---|
| 4511·27 (10*R*) | 22160·5 | 2212·6 | (1) | 22294·8 |
| 4101·72 (10*R*) | 24373·1 | | | |
| 2932·60 (6*R*) | 34089·4 | 2212·4 | (2) | 10366·0 |
| 2753·87 (6*R*) | 36301·8 | | | |
| 2601·75 (6*R*) | 38424·2 | 2212·8 | (3) | 6031·0 |
| 2460·06 (6*R*) | 40637·0 | | | |
| 2468·01 (4*R*) | 40506·2 | 2211·7 | (4) | 3949·5 |
| 2340·22 (6*R*) | 42717·9 | | | |
| 2399·25 (4*R*) | 41667·0 | 2213·6 | (5) | 2787·8 |
| 2278·2 (1*R*) | 43880·6 | | | |
| *2357·6 (1*R*) | 42403·1 | | (6) | 2068·8 |
| 2241·5 (1*R*) | 44599·1 | | | |
| $\sigma_2$ | | | | |
| 2218·2 (1*R*) | 45068 | | (7) | 1600 |
| 2199·9 (1*R*) | 45442 | | (8) | 1226 |

**Diffuse.** $1\pi - m\delta$. $1\pi_1 = 44455{\cdot}3$ ; $1\pi_2 = 46667{\cdot}9$.

| λ, Int. | ν | Δν | $m$ | $m\delta'$, δ |
|---|---|---|---|---|
| 3258·52 (6*R*) | 30679·9 | 23·5 | (2) | 13775·4 |
| 56·03 (10*R*) | 703·4 | 2212·5 | | 751·9 |
| 3039·34 (10*R*) | 32892·4 | | | |
| 2713·95 (6*R*) | 36835·8 | 49·9 | (3) | 7619·5 |
| 10·28 (10*R*) | 885·7 | 2212·5 | | 7569·6 |
| 2560·16 (8*R*) | 39048·3 | | | |
| 2522·99 (4*R*) | 39623·6 | 25·6 | (4) | 4831·8 |
| 21·36 (8*R*) | 649·2 | 2212·3 | | 06·1 |
| 2389·56 (8*R*) | 41835·9 | | | |
| 2430·7 (1*R*) | 41127·9 | 17·3 | (5) | 3328·3 |
| 29·68 (1*R*) | 145·2 | 2210·7 | | 10·1 |
| 2306·7 (1*R*) | 43338·6 | | | |
| —— | —— | | (6) | 2443·6 |
| 2379·66 (1*R*) | 42009·9 | | | 45·4 |
| 2260·5 (1*R*) | 44224·3 | | | |
| $\delta_2$ | | | | $m\delta'$ |
| 2230·8 (1*R*) | 44813 | | (7) | 1855 |
| 2211·1 (1*R*) | 45212 | | (8) | 1456 |
| 2197·4 (1*R*) | 45494 | | (9) | 1174 |
| 2187·4 (1*R*) | 45702 | | (10) | 966 |
| 2179·9 (1*R*) | 45859 | | (11) | 809 |

**In Combinations.**

| λ, Int. | ν | ν *calc.* |
|---|---|---|
| 2720·00 (2*n*) | 36753·9 | $1\pi_1 - 3\pi_1 = 36759{\cdot}8$ |
| 2565·50 (2*n*) | 38967·1 | $1\pi_2 - 3\pi_1 = 38972{\cdot}4$ |
| 2572·62 (2*r*) | 38859·3 | $1\pi_2 - 3\pi_2 = 38861{\cdot}1$ |
| 2666·23 (2) | 37495·0 | $1\pi_1 - 3\varphi = 37495{\cdot}0$† |

* λ possibly in error.

† $3\varphi$ assumed $= 6960{\cdot}3$, which is a probable value.

In DOUBLETS—*Continued.*

| *Unclassified Lines of* In.* | | | |
|---|---|---|---|
| λ, Int. | ν | λ, Int. | ν |
| 4108·84 (1*R*) | 24330·9 | 2858·19 (1) | 34976·9 |
| 3610·50 (1 ?) | 27689·1 | 58·08 (1) | 978·2 |
| 3261·06 (2 ?) | 30656·0 | 36·90 (3*R*) | 35239·4 |
| 3186·79 (1) | 31429·6 | 2775·36 (1) | 36020·7 |
| 3066·30 (1*R*) | 32603·1 | 2470·57 (2 ?) | 40464·2 |
| 51·19 (1) | 764·7 | | |
| 51·07 (4) | 765·9 | * All except the last are from Exner and Haschek. | |
| 2957·02 (2*R*) | 33808·0 | | |

has accordingly not yet been identified. As in other elements of this sub-group, nearly all the arc lines have been classified. Only one of Kayser and Runge's lines is outstanding, but twelve faint lines given by Exner and Haschek do not appear to be capable of explanation as combinations.

The spark spectrum shows some characteristic lines, but possible series have not been investigated. Rydberg, however, called attention to two pairs of lines having a separation $\Delta\nu=7926$, according to Hartley and Adeney's wave-lengths. The more accurate measures by Exner and Haschek, however, do not confirm the equality of the separations. The lines in question are (in I. A.) :—

| λ, Int. | ν | Δν |
|---|---|---|
| 3835·0 (3*n*) | 26068·3 | 7920·6 |
| 2941·28 (10) | 33988·9 | |
| 2890·24 (4) | 34589·0 | 7937·4 |
| 2350·76 (1) | 42526·4 | |

Measures of the spark spectrum on the international scale have been made by Schulemann,* covering the region λ7455—2264, and giving a large number of lines not recorded by other observers. For the above pairs, his values give the separations as 7922·74 and 7937·84.

## THALLIUM.

Tl. At. wt.=204·0 ; At. No.=81.

The series spectrum of thallium is well developed, and consists of widely-separated pairs, so that while one component of the first principal pair lies in the green, the other is in the ultra-violet. Thallium is remarkable for the easy reversal of most of the series lines.

The most complete measures of the arc spectrum are those of Paschen, and Kayser and Runge, whose wave-lengths have been adopted from the red to λ2129. Beyond this, the only published wave-lengths of the series lines are those determined by Cornu,† which are subject to considerable uncertainty. A list of wave-lengths from 3229 to 2210 has been given by Huppers,‡ but is too incomplete for our present purpose. The series are tabulated as given by Dunz, with the figures corrected to the international system, and a few additional combinations. The limits of the sub-

* Zeit. f. Wiss. Phot., **10**, 263 (1912).
† Jour. de Phys., (2) **5**, 93 (1886).
‡ Zeit. f. Wiss. Phot., **13**, 74 (1914).

## Tl Doublets.

PRINCIPAL. $1\sigma - m\pi$.
$1\sigma = 22786{\cdot}7$.

| . | ν | Δν | *m* | $m\pi_{1,2}$ |
|---|---|---|---|---|
| (10*R*) | —18684·8 | 7792·7 | (1) | 41471·5 |
| (10*R*) | —26477·5 | | | 49264·2 |
| | 8683·3 | 1001·2 | (2) | 14103·4 |
| | 7682·1 | | | 15104·6 |
| (8) | 15263·5 | 372·7 | (3) | 7523·2 |
| (6) | 14890·8 | | | 7895·9 |
| (4) | 18085·0 | 181·6 | (4) | 4701·7 |
| (2) | 17903·4 | | | 4883·3 |
| (2) | 19566·1 | 104·3 | (5) | 3220·6 |
| (1) | 461·8 | | | 3324·9 |
| (2) | 20439·6 | 63·3 | (6) | 2347·1 |
| (2) | 376·3 | | | 2410·4 |
| (1) | 20999·9 | 34·8 | (7) | 1786·8 |
| (1) | 965·1 | | | 1821·6 |
| (3) | 21370·2 | | (8) | 1416·5 |
| (2) | 21652·1 | | (9) | 1134·6 |
| (1) | 21853·7 | | (10) | 933·0 |
| (0) | 21982·0 | | (11) | 804·7 |

SHARP. $1\pi - m\sigma$.
$1\pi_1 = 41471{\cdot}5$ ; $1\pi_2 = 49264{\cdot}2$.

| :. | ν | Δν | *m* | $m\sigma$ |
|---|---|---|---|---|
| (10*R*) | 18684·8 | 7792·7 | (1) | 22786·7 |
| (10*R*) | 26477·5 | | | |
| (10*R*) | 30953·2 | 7792·8 | (2) | 10518·3 |
| (8*R*) | 38746·0 | | | |
| (8*R*) | 35373·3 | 7792·7 | (3) | 6098·2 |
| (6*R*) | 43166·0 | | | |
| (2*n*) | 37504·3 | 7790·7 | (4) | 3968·2 |
| (4*R*) | 45295·0 | | | |
| (4*R*) | 38664·4 | 7789·1 | (5) | 2808·9 |
| (1*R*) | 46453·5 | | | |
| (2*R*) | 39386·5 | | (6) | 2085·0 |
| | 47174·6 | | | |
| (1*R*) | 39861·3 | | (7) | 1610·2 |
| | 47640·1 | | | |
| (1*R*) | 40189·2 | | (8) | 1282·3 |
| | 47989·9 | | | |
| (1*R*) | 40431·5 | | (9) | 1040·0 |
| | 48240·2 | | | |
| (1*R*) | 40606·2 | | (10) | 865·3 |
| (1*R*) | 40741·0 | | (11) | 730·5 |
| (1*R*) | 40845·5 | | (12) | 626·0 |
| (1*R*) | 40935·0 | | (13) | 536·5 |

refrangible components not recorded.
ites not observed beyond this pair.
and smaller wave-lengths may be much

DIFFUSE. $1\pi - m\delta$.
$1\pi_1 = 41471{\cdot}5$ ; $1\pi_2 = 49264{\cdot}2$.

| λ, Int. | ν | Δν | *m* | $m\delta'$, δ |
|---|---|---|---|---|
| 3529·43 (8*R*) | 28325·2 | 82·0 | (2) | 13146·2 |
| 19·24 (10*R*) | 407·2 | | | 064·3 |
| | | 7793·0 | | |
| 2767·87 (10*R*) | 36118·2 | | | |
| 2921·52 (6*R*) | 34218·8 | 37·5 | (3) | 7252·8 |
| 18·32 (10*R*) | 256·3 | | | 15·2 |
| | | 7792·5 | | |
| 2379·58 (8*R*) | 42011·3 | | | |
| 2710·67 (4*R*) | 36880·4 | 19·6 | (4) | 4591·6 |
| 09·23 (8*R*) | 900·0 | | | 71·5 |
| | | 7791·6 | | |
| 2237·84 (6*R*) | 44672·0 | | | |
| 2609·77 (4*R*) | 38306·1 | 11·5 | (5) | 3165·8 |
| 08·99 (6*R*) | 317·6 | | | 53·9 |
| | | 7791·9 | | |
| 2168·61 (4*R*) | 46098·0 | | | |
| †2552·98 (2*R*) | 39158·1 | 7·0 | (6) | 2314·7 |
| 52·53 (6*R*) | 165·1 | | | 06·4 |
| | | 7790·0 | | |
| 2129·33 (1*R*) | 46948·1 | | | |
| | | | | $m\delta$ |
| 2517·41 (4*R*) | 39711·4 | | (7) | 1760·1 |
| ‡2105·0 | 47491 | | | |
| 2493·91 (2*R*) | 40085·6 | | (8) | 1385·9 |
| 2088·7 | 47861 | | | |
| 2477·49 (1*R*) | 40351·2 | | (9) | 1120·3 |
| 2077·2 | 48126 | | | |
| 2465·46 (1*R*) | 40548·0 | | (10) | 923·5 |
| 2069·1 | 48315 | | | |
| 2456·45 (1*R*) | 40696·9 | | (11) | 774·6 |
| 2062·2 | 48476 | | | |
| 2449·49 (1*R*) | 40812·5 | | (12) | 659·0 |
| 2057·2 | 48594 | | | |
| 2443·92 (1*R*) | 40905·8 | | (13) | 565·7 |
| 2053·8 | 48675 | | | |
| 2439·50 (1*R*) | 40979·6 | | (14) | 491·9 |

FUNDAMENTAL. $2\delta - m\varphi$.
$2\delta = 13064{\cdot}3$ ; $2\delta' = 13146{\cdot}2$.

| λ | ν | Δν | *m* | $m\varphi$ |
|---|---|---|---|---|
| 16340·3 | 6118·2 | 82·5 | (3) | 6945·8 |
| 16123·0 | 6200·7 | | | |
| 11594·5 | 8622·4 | 84·4 | (4) | 4440·7 |
| 11482·2 | 8706·8 | | | |
| | | | (5) | [3077·0] |
| 9170·7 | 10901·3 | | (6) | 2244·9? |

## Tl Combinations.

Combinations $1\sigma - m\delta$.
$1\sigma = 22786{\cdot}7$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 10292·3 | 9713·4 | $1\sigma - 2\delta = 9722{\cdot}4$ |
| 6420·45 (1) | 15570·9 | $1\sigma - 3\delta = 15571{\cdot}5$ |
| 5488·79 (2) | 18213·9 | $1\sigma - 4\delta = 18215{\cdot}2$ |
| 5093·28 (1) | 19628·2 | $1\sigma - 5\delta = 19632{\cdot}8$ |

Combinations $m\pi - m\sigma$.

| λ | ν | ν calc. |
|---|---|---|
| 27889·6 | 3584·6 | $2\pi_1 - 2\sigma = 3585{\cdot}1$ |
| 21803·0 | 4585·3 | $2\pi_2 - 2\sigma = 4586{\cdot}3$ |
| 12491·8 | 8003·7 | $2\pi_1 - 3\sigma = 8005{\cdot}2$ |
| 7·023μ | 1423·5 | $3\pi_1 - 3\sigma = 1425{\cdot}0$ |
| 5·559μ | 1798·6 | $3\pi_2 - 3\sigma = 1797{\cdot}7$ |

Combinations $1\pi - m\pi$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| *3652·95 (1*n*) | 27367·3 | $1\pi_1 - 2\pi_1 = 27368{\cdot}1$ |
| 2945·04 (4*r*) | 33945·5 | $1\pi_1 - 3\pi_1 = 33948{\cdot}3$ |
| †2719·10 (1) | 36766·1 | $1\pi_1 - 4\pi_1 = 36769{\cdot}8$ |
| 2977·93 (1*r*) | 33570·6 | $1\pi_1 - 3\pi_2 = 33575{\cdot}6$ |
| †2843·27 (1) | 35160·5 | $1\pi_2 - 2\pi_1 = 35160{\cdot}8$ |
| 2416·70 (1*r*) | 41366·1 | $1\pi_2 - 3\pi_2 = 41368{\cdot}3$ |

Combinations $1\pi - m\varphi$.

| λ, Int. | ν | ν calc. |
|---|---|---|
| 2895·41 (4*v*) | 34527·3 | $1\pi_1 - 3\varphi = 34525{\cdot}7$ |
| 2362·08 (2*v*) | 42322·7 | $1\pi_2 - 3\varphi = 42318{\cdot}4$ |
| 2700·2 (2*n*) | 37023·3 | $1\pi_1 - 4\varphi = 37030{\cdot}8$ |

Combinations $2\sigma - m\pi$.
$2\sigma = 10518{\cdot}3$.

| λ | ν | ν calc. |
|---|---|---|
| 33393·2 | 2993·8 | $2\sigma - 3\pi_1 = 2995{\cdot}1$ |
| 38131·0 | 2621·8 | $2\sigma - 3\pi_2 = 2622{\cdot}4$ |

Combinations $2\pi - m\delta$.

| λ | ν | ν calc. |
|---|---|---|
| 51057·9 | 1958·0 | $2\pi_2 - 2\delta' = 1958{\cdot}4$ |
| 14592·6 | 6851·0 | $2\pi_1 - 3\delta' = 6850{\cdot}6$ |
| 12736·4 | 7849·4 | $2\pi_2 - 3\delta' = 7851{\cdot}8$ |
| 10496·4 | 9524·5 | $2\pi_1 - 4\delta' = 9511{\cdot}8$ |
| 9512·4 | 10509·7 | $2\pi_2 - 4\delta' = 10513{\cdot}0$ |
| 9136·1 | 10942·6 | $2\pi_1 - 5\delta' = 10937{\cdot}6$ |
| 8376·1 | 11935·5 | $2\pi_2 - 5\delta' = 11938{\cdot}8$ |
| 14515·5 | 6887·3 | $2\pi_1 - 3\delta = 6888{\cdot}2$ |
| 10492·5 | 9528·1 | $2\pi_1 - 4\delta = 9531{\cdot}9$ |

Combinations $3\delta - m\varphi$.

| λ | ν | ν calc. |
|---|---|---|
| 3·595μ | 2781 | $3\delta - 4\varphi = 2774{\cdot}5$ |
| 3·568μ | 2803 | $3\delta' - 4\varphi = 2812{\cdot}1$ |

*Unclassified Lines of* Tl.

| λ | ν | λ | ν |
|---|---|---|---|
| 7·117μ | 1404·7 | ‡2671·10 (2*v*) | 37426·7 |
| 3·92865μ | 2544·7 | 2669·95 (1) | 37442·8 |
| 3·92155 | 2549·3 | 2577·67 (1) | 38783·1 |
| 2·70276? | 3698·9 | 2532·71 (1*n*) | 39471·6 |
| 2·70237 | 3699·4 | 2530·80 (1*n*) | 39501·3 |
| 2·13979 | 4672·1 | 2512·59 (1) | 39787·5 |
| 2·04858 | 4880·1 | 2434·05 (1) | 41071·3 |
| 1·45978 | 6848·5 | 2417·01 (2) | 41360·8 |
| 1·16907 | 8551·4 | | |
| 3230·6 (1) | 30945·1 | | |
| 2210·73 (2*R*) | 45219·8 | | |

* Not given by Dunz.
† Given by Huppers.
‡ This and succeeding lines are given by Huppers, not by Kayser and Runge. The first, second, fifth, and seventh are given in spark by Eder and Valenta.

ordinate series were calculated by Dunz from the sharp series. It will be seen that nearly all the lines are included in the recognised series.

The enhanced lines do not appear to have been investigated for series relationships. The vacuum-arc and spark spectra in the region λ1908 to λ1477 have been observed by McLennan.*

The sharp series is not well represented by most of the ordinary formulæ. For wave-numbers on the Rowland system, however, Johanson has obtained a fair agreement by his formula (*see* p. 36) with the constants $A = 41469{\cdot}33$ ; $\mu = 2{\cdot}261774$ ; $a = 1{\cdot}672006$ ; $b = -1{\cdot}937964$.

* Proc. Roy. Soc., A. **98**, 108 (1920).

# CHAPTER XVIII.

## ELEMENTS OF GROUPS IV. AND V.

### ELEMENTS OF GROUP IV.

There are no published records of the discovery of typical series in the spectra of any of the elements of this group. Constant difference groups, however, were found by Kayser and Runge in the spectra of lead and tin which have been verified with remarkable accuracy in Kayser's laboratory by Klein* and Arnolds† respectively. In the arc spectrum of lead there are 10 lines differing in wave-number by 10807·43 from 10 other lines, and these, again, by 2831·2 from other more refrangible lines. Similarly, for the arc lines of tin there are 10 sets of three lines for which the separations are 5185·43 and 1735·84.

In the spectrum of tin Lohuizen‡ has suggested two groups of parallel series, which he has called "translation series." Thus, he gives six series with limits 45307·40, 50494·43, 50926·14, 52330·66, 53507·27, 53924·00, for all of which the terms "$mx$" are given by $N/(m+1{\cdot}651360-657{\cdot}42\lambda^{-1})^2$; and three series having limits 43825·00, 49012·03, 50748·26, with the variable terms given by $N/(m+1{\cdot}384406+446{\cdot}70\lambda^{-1})^2$. The number of lines in a series ranges from three to five.

In germanium (Ge. At. wt.=72·5; At. No.=32) Paulson finds three triplets with separations of 1416, 903, and two pairs with a separation equal to the sum of these.

Constant difference pairs have also been noted by Paulson among the arc lines of titanium, with separations of 71, 64, 779, or 1166. Only a small proportion of the lines of this element are included.

As regards the remaining elements of Group IV., carbon and silicon, some unpublished results obtained by the writer are of interest and may be briefly mentioned.

*Carbon* (C. At. wt.=12·0; At. No.=6).—The arc spectrum of carbon shows only one line, $\lambda$2478, in the whole range of spectrum from the extreme red to $\lambda$2000. It is possible that there may be other arc lines in the Schumann region, but the spectrum has not been obtained under conditions which permit them to be distinguished as such with certainty. Observations in this region have been made by Wolff,§ McLennan,‖ and Millikan.¶

In the spark spectrum of carbon, $C^+$, the writer has established doublet series for which $\Delta\nu=10{\cdot}8$ and which have $4N$ for the series constant as in other series of ionised elements. With greater energy, a triplet is developed near $\lambda$4647, having $\Delta\nu=13{\cdot}0$, 5·5; this may possibly represent $C^{++}$, or the second-step ionisation, but it has not yet been possible to prove this by establishing the triplet as a member of a system of series having $9N$ for constant. With the greatest energy, as Merton**

* Zeit. f. Wiss. Phot., **12**, 16 (1913).
† *Ibid.*, **13**, 313 (1913).
‡ Proc. Roy. Acad. Amsterdam, April, 1912.
§ Ann. d. Phys., **42**, 837 (1913).
‖ Proc. Roy. Soc., A. **95**, 272, 327 (1919).
¶ Astrophys. Jour., **52**, 59 (1920).
** Proc. Roy. Soc., A. **91**, 498 (1915).

has shown, certain other lines are developed in the carbon spectrum which correspond with lines in the spectra of Wolf-Rayet stars. The wave-lengths of the most prominent of these are 5812 and 5801, forming a pair with $\Delta\nu=31{\cdot}4$. This may perhaps represent a third-step ionisation, but the evidence for this is not complete.

*Silicon* (Si. At. wt.=28·3; At. No.=14).—Lockyer has shown that successive spectra are developed in this element as the energy of excitation is increased, and he has designated them Si I., Si II., Si III., and Si IV., the first representing the arc spectrum. These observations, however, covered too restricted a range of spectrum for the investigation of series, and have been extended by the writer.

Evidence has been obtained that the arc spectrum, Si I., includes a system of triplets, in which $\Delta\nu=146$, 77. There is a diffuse triplet, with a normal set of satellites, a normal sharp triplet, certain other triplets not yet classified, and a number of pairs having separations of 146 or 77. Series formulæ have not been calculated, but the lines in question are undoubted arc lines.

The spark spectrum, Si II., shows a system of doublets in which $\Delta\nu=60{\cdot}0$. The principal, sharp, and diffuse series are well represented in the spectrum under suitable conditions of experiment, and the series constant for them is definitely $4N$. The doublets are therefore to be assigned to ionised silicon, $Si^{+}$.

Additional triplets associated with that observed in Si III. by Lockyer have been obtained, but not yet in sufficient number to allow of the definite calculation of the series constant. It is not improbable, however, that the triplets represent the second-step ionisation, for which the constant would be $9N$, and they may be provisionally assigned to $Si^{++}$.

Lockyer's Si IV. was represented by a well-known pair in the violet. The separation $\Delta\nu$ is 164, and three other pairs with the same separation have now been found in the ultra-violet. Further observations in the Schumann region may establish the character of these pairs, but meanwhile it may be supposed possible that they represent the third-step ionisation, $Si^{+++}$.

It should be noted that the separations of the doublets and triplets in the successive spectra of silicon are related to the corresponding separations in carbon in very close proportion to the squares of the atomic weights.

These observations of carbon and silicon are of special interest in connection with Kossel and Sommerfeld's displacement law to which reference has already been made (p. 74).

## Elements of Group V.

No series have been identified in any of the elements of this group. Constant difference lines, however, were noted by Kayser and Runge in the spectra of arsenic, antimony and bismuth, and in other elements of the group by Paulson. In all cases, the constant separations refer to pairs of lines, two or more separations being involved.

It is scarcely possible to summarise the data usefully, and reference must be made to the original sources.*

In the case of nitrogen, it should be observed that Stark and Hardtke† have obtained a spectrum which they have described as the arc spectrum. The more familiar line spectrum thus becomes the probable spark spectrum, $N^{+}$. Prior to Hardtke's work, certain lines developed under a more powerful stimulus were

* Kayser's Handbuch, Vol. II., and Paulson's papers previously quoted.
† Ann. d. Phys., **56**, 363 (1918.)

obtained by Lockyer, Baxandall, and Butler, and described as the enhanced lines of nitrogen. This spectrum was afterwards described more completely by Fowler,* and should, perhaps, be considered to represent the second-step ionisation, or $N^{++}$. The matter is of some importance in connection with Kossel and Sommerfeld's suggestive displacement law, and the following particulars of pairs of lines may be quoted :—

| | $\lambda$ I.A. | $\nu$ | $\Delta\nu$ |
|---|---|---|---|
| Probable principal pair ... ... | 4097·33 (10)<br>4103·39 (8) | 24399·30<br>363·22 | 36·08 |
| Probable diffuse pair ... ... ... | 4641·91 (3)<br>40·65 (10)<br>34·17 (8) | 21536·84<br>542·70<br>572·83 | 5·86<br>35·99 |
| Possible sharp pair ... ... ... | 4867·14 (4)<br>58·82 (3) | 20540·23<br>575·40 | 35·17 |

The measures of the last pair are less satisfactory than those of the first two.

* Monthly Notices R.A.S., **80**, 692 (1920).

# CHAPTER XIX.

## GROUP VI.—OXYGEN, SULPHUR, AND SELENIUM.

Our knowledge of the series lines of the elements of this sub-group is due to Runge and Paschen.* Each element shows two distinct line spectra, which are well known under the names of the "compound line" and "elementary line" spectra. These names were assigned to the oxygen spectra by Schuster,† and were adopted by Kayser for the corresponding spectra of sulphur and selenium. The two spectra are developed respectively by uncondensed discharges and condensed discharges of moderate intensity, and the names given by Schuster were based upon the supposition that complex and simplified molecular groupings were involved in the two cases. The compound line spectra were distinguished as the "series spectra" of the respective elements by Runge and Paschen.

When powerful condensed discharges are employed, a third system of lines is produced in oxygen‡ and sulphur,§ and it would seem convenient, provisionally, to follow the plan adopted by Lockyer in the case of silicon, and to distinguish the compound line, the elementary line and the third line spectra by adding I, II, III to the chemical symbol of the element, as O. I, O. II, O. III, &c. In general terms, the three spectra have been described as the arc, spark and super-spark spectra. Intermediate stages may be readily obtained by suitable adjustment of the gas pressure, diameter of capillary tube and intensity of discharge.

It is only in the first line spectra that series have at present been identified.

### OXYGEN.

O. At. wt.=16·00; At. No.=8.

The compound line, or O. I, spectrum of oxygen exhibits a system of narrow triplets, and a system which was at first described as consisting of doublets. The latter, however, were only partially resolved, and the separation was only given for one line of the sharp series, namely :—

$$\begin{array}{l} \lambda 6046{\cdot}348\ (7) = \nu 16534{\cdot}34 \\ \lambda 6046{\cdot}120\ (2) = \nu 16534{\cdot}97 \end{array} \qquad \Delta\nu = 0{\cdot}63$$

Since most other spectra which show triplets also show singlet series, but never doublets, it is possible that the oxygen series in question may really consist of single lines.‖ They have been entered as singlets in the table.

The first principal triplet shows separations $\Delta\nu = 3{\cdot}4$, $2{\cdot}7$, according to the

* Ann. d. Phys., **61**, 641 (1897); Astrophys. Jour., **8**, 70 (1898).
† Phil. Trans., **170**, 41 (1879).
‡ Fowler and Brooksbank, Monthly Not. R.A.S., **77**, 511 (1917).
§ Lockyer, Proc. Roy. Soc., A. **80**, 55 (1907).
‖ See also Sommerfeld, Ann. d. Phys., **63**, 224 (1920). Recent investigations by Dr. Catalán, however, have suggested that the members of this system may be very narrow triplets.

measures of Runge and Paschen; the more recent determinations by Meggers and Kiess* are

| $\lambda$ | $\nu$ | $\Delta\nu$ |
|---|---|---|
| 7771·928 | 12863·28 | |
| 74·138 | 859·62 | 3·66 |
| 75·433 | 857·49 | 2·13 |

and the intervals are thus brought into closer accordance with the separations of the triplets of the subordinate series. It may be recalled that the principal triplet occurs in the solar spectrum, and has its origin in the solar atmosphere.

The limits given in the tables have been adapted from those calculated for the sharp series by Dunz. The fundamental series should be in the infra-red, where observations have not yet been made.

Among the unclassified lines of O. I are two "inverted" wider triplets, with mean separations 7·7 and 12·6, which Hicks† has suggested may be united with $\lambda$5037 of the *D* series in a "new diffuse series," for which he has calculated the limit 22926.

A considerable number of lines of O. I have been observed in the ultra-violet by Schniederjost,‡ but their relation to the established series, if any, has not yet been traced. The wave-lengths of these lines are included in the table of unclassified lines.

In the spectrum of O. II, six pairs of lines, with separation $\Delta\nu=179{\cdot}9$, have been identified by the writer, but the series arrangement remains to be discovered.

O "SINGLETS."

PRINCIPAL. $1S—mP$. $1S=33043{\cdot}3$.

| λ, Int. | ν | *m* | *mP* |
|---|---|---|---|
| 8446·38 | 11836·1 | (1) | 21207·2 |
| 4368·30 (10) | 22885·8 | (2) | 10157·5 |
| 3692·44 (7) | 27074·7 | (3) | 5968·6 |

SHARP. $1P—mS$. $1P=21207{\cdot}2$.

| λ, Int. | ν | *m* | *mS* |
|---|---|---|---|
| — 8446·38 | —11836·1 | (1) | 33043·3 |
| 13163·7 | 7594·7 | (2) | 13612·5 |
| 7254·05 (2) | 13781·6 | (3) | 7425·6 |
| 6046·34 (7*d*) | 16534·4 | (4) | 4672·8 |
| 5554·94 (6*d*) | 17997·0 | (5) | 3210·2 |
| 5299·00 (5) | 18866·3 | (6) | 2340·9 |
| 5146·06 (5) | 19426·9 | (7) | 1780·3 |
| 5047·70 (2*n*) | 19805·5 | (8) | 1401·7 |
| 4979·55 (1*n*) | 20076·6 | (9) | 1130·6 |

DIFFUSE. $1P—mD$. $1P=21207{\cdot}2$.

| λ, Int. | ν | *m* | *mD* |
|---|---|---|---|
| 11287·3 | 8857·2 | (2) | 12350·0 |
| 7002·22 (4) | 14277·3 | (3) | 6929·9 |
| 5958·53 (6*d*) | 16778·0 | (4) | 4429·2 |
| 5512·71 (5*d*) | 18134·9 | (5) | 3072·3 |
| 5275·08 (4) | 18951·8 | (6) | 2255·4 |
| 5130·53 (3) | 19485·8 | (7) | 1721·4 |
| 5037·16 (2*n*) | 19846·9 | (8) | 1360·3 |
| 4972·87 (1*n*) | 20103·5 | (9) | 1103·7 |

* Scientific Papers, Bureau of Standards, Washington, No. 324, p. 644 (1918).
† Phil. Trans., A., **213**, 368 (1914).
‡ Zeit. f. Wiss. Phot., **2**, 266 (1904).

## O Triplets.

**Principal.** $1s—mp$. $1s=36069\cdot0$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| 7771·97 (10) | 12863·2 | 3·4 | (1) | 23205·8 |
| 74·01 (8) | 859·8 | 2·7 | | 209·2 |
| 75·68 (6) | 857·1 | | | 211·9 |
| 3947·33 (10) | 25326·5 | 1·2 | (2) | 10742·5 |
| 47·51 (7) | 325·3 | 0·6 | | 743·7 |
| 47·61 (4) | 324·7 | | | 734·3 |

**Sharp.** $1p—ms$. $1p_1=23205\cdot8$ ; $1p_2=23209\cdot2$ ; $1p_3=23211\cdot9$.

| λ, Int. | ν | Δν | $m$ | $ms$ |
|---|---|---|---|---|
| —7771·97 | —12863·2 | 3·4 | (1) | 36069·0 |
| — 74·01 | — 859·8 | 2·7 | | |
| — 75·68 | — 857·1 | | | |
| 11300 | 8847·3 | | (2) | 14358·5 |
| 294 | 8852·0 | | | |
| 294 | 8852·0 | | | |
| 6456·07 (9) | 15485·0 | 3·7 | (3) | 7720·8 |
| 54·55 (7) | 488·7 | 2·0 | | |
| 53·69 (6) | 490·7 | | | |
| 5436·83 (8) | 18388·0 | 3·5 | (4) | 4817·9 |
| 35·78 (6) | 391·5 | 2·1 | | |
| 35·16 (5) | 393·6 | | | |
| 5020·13 (5) | 19914·3 | 3·1 | (5) | 3291·9 |
| 19·34 (4) | 917·4 | 2·2 | | |
| 18·78 (3) | 919·6 | | | |
| 4803·00 (4) | 20814·5 | 3·5 | (6) | 2391·6 |
| 02·20 (3) | 818·0 | 1·7 | | |
| 01·80 (2) | 819·7 | | | |
| 4673·70 (3) | 21390·4 | | (7) | 1815·7 |
| 72·75 } (3*d*) | 394·7 | | | |
| 72·75 } | 394·7 | | | |
| 4589·89 (3) | 21780·9 | | (8) | 1425·1 |
| 88·98 } (2*d*) | 785·3 | | | |
| 88·98 } | 785·3 | | | |

**Diffuse.** $1p—md$. $1p_1=23205\cdot8$ ; $1p_2=23209\cdot2$ ; $1p_3=23211\cdot9$.

| λ, Int. | ν | Δν | $m$ | $md$ |
|---|---|---|---|---|
| [9266·57] | 10788·5 | | (2) | 12417·3 |
| 9263·88 | 791·7 | | | |
| 6158·20 (10) | 16234·0 | 3·8 | (3) | 6971·7 |
| 56·78 (8) | 237·8 | 2·1 | | |
| 55·99 (7) | 239·9 | | | |
| 5330·66 (10) | 18754·2 | 3·8 | (4) | 4451·5 |
| 29·59 (7) | 58·0 | 2·1 | | |
| 28·98 (6) | 60·1 | | | |
| 4968·76 (6) | 20120·2 | 3·6 | (5) | 3085·7 |
| 67·86 (5) | 123·8 | 1·9 | | |
| 67·40 (4) | 125·7 | | | |
| 4773·76 (5) | 20942·0 | 3·8 | (6) | 2263·9 |
| 72·89 (4) | 945·8 | 1·6 | | |
| 72·54 (3) | 947·4 | | | |
| 4655·36 (4) | 21474·6 | 3·7 | (7) | 1731·4 |
| 54·56 (3) | 478·3 | 1·5 | | |
| 54·23 (2) | 479·8 | | | |
| 4577·66 (3) | 21839·1 | | (8) | 1367·1 |
| 76·79 (2*d*) | 843·3 | | | |
| 4523·53 | 22100·5 | | 9) | 1106·1 |
| 22·78 (*d*) | 104·1 | | | |

O TRIPLETS—*Continued.*

*Unclassified Lines of* O. I.

(Runge & Paschen.)

| λ, Int. | ν | Δν |
|---|---|---|
| 6266·85 (1) | 15952·6 | |
| 64·57 (1) | 958·4 | 7·9 |
| 61·47 (3) | 966·3 | 12·4 |
| 56·60 (1) | 978·7 | |
| 5995·48 (4) | 16674·6 | |
| 92·45 (3) | 683·0 | |
| 50·60 (5) | 800·4 | |
| 5410·76 (3) | 18476·6 | 7·4 |
| 08·59 (4) | 484·0 | 12·7 |
| 04·87 (3) | 496·7 | |
| 4233·32 | 23615·5 | |
| 22·78 | 674·4 | |
| 17·09 | 706·4 | |
| 3830·26 | 26100·5 | |
| 25·07 | 135·9 | |
| 23·56 | 146·3 | |
| 2883·84 | 34665·9 | |

* Pop. Ast., **29**, 19 (1921).

(Schniederjost.)

| λ, Int. | λ | λ |
|---|---|---|
| 2897·31 (2*n*) | 2672·79 (1) | 2352·53 (2) |
| 95·26 (3) | 38·90 (2) | 25·26 (3) |
| 83·82 (4) | 07·42 (2) | 2299·86 (3) |
| 81·74 (2*n*) | 2577·84 (2) | 14·55 (2) |
| 58·70 (1) | 50·55 (1) | 2189·92 (2) |
| 2786·07 (1) | 04·58 (2) | 37·5 (1) |
| 53·37 (1) | 2474·37 (2) | 12·3 (1) |
| 23·47 (1) | 45·97 (3) | |
| 08·08 (1) | 19·56 (3) | |

*Oxygen Lines in infra-red** (Kiess).

| λ, Int. | ν | Δν |
|---|---|---|
| 8233·05 (<1) | 12142·83 | |
| 30·05 (<1) | 147·25 | 4·42 |
| 21·84 (1) | 159·39 | 12·14 |
| 7952·22 (<1) | 12571·66 | |
| 50·84 (1) | 573·84 | 2·18 |
| 47·58 (2) | 578·99 | 5·15 |
| 7481·27 (<1) | 13363·04 | |
| 79·23 (<1) | 366·68 | 3·64 |
| 76·58 (1) | 371·42 | 4·74 |

SULPHUR.

S. At. wt.=32·07 ; At. No.=16.

The compound line spectrum of sulphur (S. I) is found only in vacuum tube observations. Nearly all the lines are included in a system of triplets resembling those of O. I, but having a wider separation. Some of the earlier members of the series have not yet been observed. The limits of *s* and *d* have been adapted from those given by Dunz.

It should be noted that the *p* series is not indicated by Dunz, and that the first *p* triplet, which lies in the infra-red and outside the range of the observations, has been calculated from the Rydberg relations. Thus, the limit $1p_1$ having been determined from the *d* series, we have

$$20085{\cdot}5 = 1p_1 = N/(1+p_1)^2$$
$$\therefore\ p_1 = 1{\cdot}336781$$
$$N/(2+p_1)^2 = 2p_1 = 9850{\cdot}7$$
$$\text{Observed } p_1(2) = 1s - 2p_1 = 21297{\cdot}0$$
$$\therefore\ 1s = 31147{\cdot}7$$
$$1p_1 = 20085{\cdot}5$$
$$\text{Calculated } p_1(1) = 11062{\cdot}2$$

The position thus assigned to $p_1(1)$ depends solely upon the Rydberg formula, and is probably not exact, but it might have been sufficiently near to suggest a combination which would have indicated the necessary correction.

S TRIPLETS.

PRINCIPAL. $1s—mp$.
$1s=[31147{\cdot}7]$.

| λ, Int. | ν | Δν | *m* | $mp_{1,2,3}$ |
|---|---|---|---|---|
| | [11062·2] | 17·9 | (1) | 20085·5 |
| | [ 044·3] | 11·3 | | 103·4 |
| | [ 033·0] | | | 114·7 |
| 4694·18 (10) | 21297·0 | 6·0 | (2) | [9850·7] |
| 95·51 (8) | 291·0 | 3·6 | | [ 56·7] |
| 96·31 (6) | 287·4 | | | [ 60·3] |

SHARP. $1p—ms$.
$1p_1=20085{\cdot}5$ ; $1p_2=20103{\cdot}4$ ; $1p_3=20114{\cdot}7$.

| λ, Int. | ν | Δν | *m* | *ms* |
|---|---|---|---|---|
| 6415·47 (4) | 15583·0 | 17·9 | (4) | 4502·5 |
| 08·11 (3) | 600·9 | 11·3 | | |
| 03·49 (2) | 612·2 | | | |
| 5889·86 (2) | 16973·6 | 18·3 | (5) | 3111·6 |
| 83·52 (2) | 991·9 | 11·4 | | |
| 79·57 (1) | 17003·3 | | | |
| 5614·26 (5) | 17806·9 | 17·8 | (6) | 2278·9 |
| 08·65 (4) | 824·7 | 10·6 | | |
| 05·30 (3) | 835·3 | | | |
| 5449·78 (3) | 18344·3 | 18·2 | (7) | 1741·1 |
| 44·37 (2) | 362·5 | | | |

*Unclassified Lines of* S.

| λ, Int. | ν | Δν |
|---|---|---|
| 7241·7 (2) | 13805·1 | |
| 6538·60 (1) | 15289·6 | 5·3 |
| 36·33 (1) | 294·9 | |
| 6396·69 (1) | 15628·8 | 4·4 |
| 94·89 (1) | 633·2 | |

DIFFUSE. $1p—md$.
$1p_1=20085{\cdot}5$ ; $1p_2=20103{\cdot}4$ ; $1p_3=20114{\cdot}7$.

| λ, Int. | ν | Δν | *m* | *md* |
|---|---|---|---|---|
| 6757·16 (7) | 14795·1 | 18·2 | (4) | 5290·2 |
| 48·83 (6) | 813·3 | 11·3 | | |
| 43·69 (5) | 824·6 | | | |
| 6052·75 (7) | 16516·9 | 18·4 | (5) | 3568·3 |
| 46·01 (6) | 535·3 | 11·1 | | |
| 41·95 (5) | 546·4 | | | |
| 5706·22 (8) | 17519·9 | 18·0 | (6) | 2565·7 |
| 00·36 (7) | 537·9 | 10·9 | | |
| 5696·80 (6) | 548·8 | | | |
| 5506·98 (5) | 18153·7 | 17·9 | (7) | 1931·8 |
| 01·56 (3) | 171·6 | 11·3 | | |
| 5498·16 (3) | 182·9 | | | |
| 5380·99 (4) | 18578·8 | 18·0 | (8) | 1506·8 |
| 75·78 (3) | 596·8 | 10·9 | | |
| 72·62 (2) | 607·7 | | | |
| 5295·69 (4) | 18878·0 | 17·8 | (9) | 1207·8 |
| 90·72 (4) | 895·8 | 10·7 | | |
| 87·71 (2) | 906·5 | | | |

*Unclassified Lines of* S—*continued*.

| λ, Int. | ν | Δν |
|---|---|---|
| 6175·80 (1) | 16187·8 | 5·8 |
| 73·56 (1) | 193·6 | |
| *5279·02 (6) | 18937·6 | 1·4 |
| 78·64 (5) | 939·0 | 1·8 |
| 78·14 (3) | 40·8 | |

* Compare with isolated triple group in Se.

SELENIUM.

Se. At. wt.=79·2; At. No.=34.

The compound line spectrum of selenium (Se I.) generally resembles the corresponding spectrum of sulphur. In the diffuse series of triplets, however, many of the brighter components are accompanied by fainter lines or satellites which are not arranged in the normal way. The first line of a triplet appears to

## Se Triplets.

### Principal. $1s—mp$.
$1s=[30699\cdot0]$.

| λ, Int. | ν | Δν | $m$ | $mp_{1,2,3}$ |
|---|---|---|---|---|
| | [11431·3] | | (1) | 19267·7 |
| | [ 327·6] | | | 371·4 |
| | [ 282·8] | | | 416·2 |
| 4731·04(10) | 21131·9 | 36·7 | (2) | [9567·1] |
| 39·28(9) | 095·2 | 14·4 | | [9603·8] |
| 42·58(8) | 080·8 | | | [9618·2] |

### Sharp. $1p—ms$.
$1p_1=19267\cdot7$ ; $1p_2=19371\cdot4$ ; $1p_3=19416\cdot2$.

| λ, Int. | ν | Δν | $m$ | $ms$ |
|---|---|---|---|---|
| 6746·42(6) | 14818·6 | 103·7 | (4) | 4449·1 |
| 6699·55(6) | 922·3 | 44·8 | | |
| 79·49(5) | 967·1 | | | |
| 6177·66(3) | 16182·9 | 103·7 | (5) | 3085·0 |
| 38·30(2) | 286·6 | 44·1 | | |
| 21·74(2) | 330·7 | | | |
| 5878·66(2) | 17006·0 | 104·0 | (6) | 2261·5 |
| 42·88(2) | 110·0 | 44·7 | | |
| 27·68(1) | 154·7 | | | |
| 5700·10(3) | 17538·7 | 103·3 | (7) | 1729·3 |
| 5666·73(3) | 642·0 | 44·7 | | |
| 52·40(3) | 686·7 | | | |

### † *Unclassified Lines of* Se I.

| λ, Int. | ν | Δν |
|---|---|---|
| 6831·04(5) | 14635·0 | |
| 6701·06(1) | 14918·9 | |
| 6283·33(2) | 15910·8 | |
| 6135·31(1) | 16294·6 | |
| 5866·31(2) | 17041·8 | |
| 5374·08(10) | 18602·7 | 14·6 |
| 5369·85(10) | 18617·3 | 15·5 |
| 5365·40 (8) | 18632·8 | |

* Lines tabulated for diffuse series by Dunz.

† Some of the lines tabulated under diffuse series should possibly be included under this head.

### Diffuse. $1p—md$.
$1p_1=19267\cdot7$ ; $1p_2=19371\cdot4$ ; $1p_3=19416\cdot2$.

| λ, Int. | ν | Δν | $m$ | $md$ |
|---|---|---|---|---|
| 7061·88(5) | 14156·7* | 103·5 | (4) | 5112·5 |
| 7013·98(3) | 14253·3 | | | |
| 10·58(3) | 260·2* | 40·6 | | |
| 6990·71(4*d*?) | 14300·8* | | | |
| 6325·60(6) | 15804·4 | 103·7 | (5) | 3462·1 |
| 25·2 (1) | 805·4* | | | |
| 6284·30(3) | 15908·3 | 45·3 | | |
| 83·98(1) | 909·1* | | | |
| 6269·07(3) | 15946·9 | | | |
| 66·15(4) | 954·4* | | | |
| 5961·86(5) | 16768·7 | 103·5 | (6) | 2498·2 |
| 61·5 (1) | 769·7* | | | |
| 5925·09(1) | 16872·7 | 44·7 | | |
| 24·91(4) | 873·2* | | | |
| 5909·27(2) | 16917·9* | | | |
| 06·88(2) | 924·7 | | | |
| 5753·30(7) | 17376·5 | 103·4 | (7) | 1887·9 |
| 52·09(2) | 380·2* | | | |
| 5718·3 (1) | 17482·9 | 44·2 | | |
| 18·06(7) | 483·6* | | | |
| 5704·96(3) | 17523·8 | | | |
| 03·64(4) | 527·8* | | | |
| 5617·83(5) | 17795·5* | 103·9 | (8) | 1472·2 |
| 5528·42(4) | 18083·3* | | (9) | 1184·3 |
| 5496·85(3) | 18187·2* | | | |
| 5464·61(3) | 18294·5 | | (10) | 973·2 |

have a satellite on the more refrangible side, while the second has a satellite on the less refrangible side; the third line in three of the triplets also has a companion of nearly the same brightness as itself.

The normal triplet separations of the sharp series are found in the diffuse series, as shown in the table, but a satisfactory interpretation of the relationships of the remaining components has not been reached. The observations of $d(4)$ may be considered incomplete, as are also those of $d(8)$, $d(9)$, and $d(10)$. Those of $d_1(5)$, $d_1(6)$, and $d_1(7)$ suggest that in the first member of the triplet the satellite occupies the normal position, while the chief component is abnormally displaced to the red. A similar abnormal displacement is shown by $d_2(5)$, but $d_2(6)$ and $d_2(7)$ show the chief line in the normal position and the satellite displaced to the red. The third member in $d(5)$ and $d(7)$ has its companion on the red side, but in $d_3(6)$ the companion is on the violet side. There is no very marked regularity in the separations of the chief lines and their companions.

The limits of $s$ and $d$ have been adopted from Dunz, with a small correction for the change to the international scale. The limit of the principal series has been calculated as in the case of sulphur.

The vacuum arc spectrum of selenium in the region $\lambda 2296-\lambda 1432$ has been observed by McLennan.*

## Other Elements of Group VI.

Constant difference pairs have been noted by Paulson in molybdenum and tungsten, but no regular series have been recognised. Some of the spectra are extremely complicated.

* Proc. Roy. Soc., A. **98**, 103 (1920).

# CHAPTER XX.

## ELEMENTS OF GROUPS VII. AND VIII.

*Elements of Group VII.*—Little progress has been made in the analysis of the spectra of the elements of this group.

Measures of fluorine of sufficient accuracy do not extend over a large range, and further investigations are much to be desired. There are some narrow triplets in the spectrum, which are produced under experimental conditions suggesting that they may belong to the ionised atoms.

Chlorine, according to Paulson, shows a few triplets with $\Delta\nu$=about 67, 41, and some pairs with one or other of these separations, or their sum. The proper classification of the lines as arc or enhanced lines calls for further experimental investigation.

Paulson has found numerous constant difference pairs in bromine and iodine.

The arc spectrum of manganese, as shown by Kayser and Runge, appears to include a system of triplets, of which they recognised five members. The wavelengths given below are from an extensive investigation of the manganese arc spectrum by Fuchs.* The members of the first diffuse triplet are involved in groups of lines, and it is doubtful which of the components should be taken. Several are entered in the table, and the $\Delta\nu$ correspond with the lines marked with an asterisk. The entire spectrum contains many hundreds of lines, and the series call for further investigation.

A few constant difference pairs, and two narrow triplets with separations 14·2 and 8·7 have been noted by Paulson.

Mn TRIPLETS.

| SHARP. $1p$—$ms$. $1p_1$=41224·4 ; $1p_2$=41398·1 ; $1p_3$=41527·2. | | | | | DIFFUSE. $1p$—$md$. $1p_1$=41224·4 ; $1p_2$=41398·1 ; $1p_3$=41527·2. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| λ, Int. | ν | Δν | $m$ | $ms$ | λ, Int. | ν | Δν | $m$ | $md$ |
| 4823·52 (10) | 20726·0 | 173·7 | (2) | 20498·4 | 3570·10(4$R$) | 28002·4* | | (2) | 13222·4 |
| 4783·43 (8) | 20899·7 | 129·1 | | | 3569·80(8$R$) | 28004·8 | | | |
| 4754·05 (10) | 21028·8 | | | | 3569·50(6$R$) | 28007·1 | 173·1 | | |
| | | | | | 3548·17(4$R$) | 28175·5* | | | |
| 3178·51 (8$n$) | 31452·2 | 173·7 | (3) | 9772·2 | 3548·02(4$R$) | 28176·7 | 129·0 | | |
| 3161·06 (4) | 31625·9 | 129·2 | | | | | | | |
| 3148·19 (4) | 31755·1 | | | | 3532·11(5$R$) | 28303·6 | | | |
| | | | | | 3532·00(5$R$) | 28304·5* | | | |
| | | | | | 3531·84(4$R$) | 28305·8 | | | |
| | | | | | 2940·40(6$n$) | 33999·0 | 172·2 | (3) | 7226 6 |
| | | | | | 2925·59(6$n$) | 34171·2 | 128·6 | | |
| | | | | | 2914·62(8$n$) | 34299·8 | | | |
| | | | | | 2726·15(4$n$) | 36670·9 | 173·1 | (4) | 4554·4 |
| | | | | | 2713·35(3$n$) | 36844·0 | 127·6 | | |
| | | | | | 2703·98(3$n$) | 36971·6 | | | |

*Elements of Group VIII.*—No series have been detected in any of the elements of this group, but Paulson has found many constant difference groups, the details of which are too extensive for quotation.

* Zeit. f. Wiss. Phot., **14**, 239, 263 (1915).

# CHAPTER XXI.

## THE INERT GASES.

In addition to helium this group of elements includes neon, argon, krypton, xenon and niton (radium emanation). The spectra are very complex, and it is only in the case of neon that series arrangements have been disentangled. In argon, krypton and xenon, however, it has been found possible to arrange many of the lines in groups showing constant differences of wave-number.

The spectra of neon, argon, krypton and xenon have been discussed at great length by Hicks,* following his own special methods, but the results cannot be briefly summarised.

### NEON.

Ne. At. wt. = 20·2 ; At. No. = 10.

The first extensive measures of the lines of neon were made by Baly,† who observed more than 800 lines in the region $\lambda$ 7000 to $\lambda$ 3500. Accurate measures of the lines in the less refrangible part of the spectrum have since been made by Meissner,‡ and also of many lines in this region by Burns, Meggers and Merrill,§ many of which are interferometer determinations. Several hundreds of lines have also lately been accurately measured by Paschen.

Watson|| was the first to note that many of the strong lines of neon could be arranged in groups of three or four, having constant wave-number separations. These are exhibited with remarkable accuracy by the Washington measures. Fifteen groups of such lines were found, of which seven are complete quadruplets ; five lack the second member, one lacks the third, and in two the second and fourth members are wanting. Three examples may be quoted :

| $\lambda$, Int. | $\nu_{1-4}$ | $\Delta\nu$ |
|---|---|---|
| 8082·45 (3) | 12369·09 | |
| 7438·902 (6) | 13439·149 | 1070·06 |
| 7245·167 (8) | 13798·507 | 359·36 |
| 7032·413 (9) | 14215·957 | 417·45 |
| 7024·049 (3) | 14232·885 | |
| 6532·883 (4) | 15302·958 | 1070·073 |
| 6382·991 (8) | 15662·316 | 359·358 |
| 6217·280 (4) | 16079·765 | 417·449 |
| 6717·043 (5) | 14883·402 | |
| 6266·495 (7) | 15953·481 | 1070·079 |
| 6128·44 (3) | 16312·87 | 359·39 |
| 5975·534 (4) | 16730·282 | 417·41 |

Two sets of apparent doublet series were traced by Rossi¶ with separation about

* Phil. Trans., A. **220**, 335-468 (1920).
† Phil. Trans., A. **202**, 183 (1904).
‡ Ann. d. Phys., **51**, 115 (1916) ; **58**, 333 (1919). Phys. Zeit., **17**, 549 (1916).
§ Scientific Papers, Bureau of Standards, Washington, No. 329 (1918).
|| Astrophys. Jour., **33**, 399 (1911).
¶ Phil. Mag., **26**, 981 (1913).

167 and converging to the same limits near 24105 and 24272. Several additional series were afterwards recognised by Meissner. All these are included in a masterly analysis of the neon spectrum which has been set forth by Paschen in two recent papers.* The spectrum differs from those which have previously been described in having an extraordinarily large number of series. Thus, Paschen finds four series of $s$ terms, ten of $p$ terms, and twelve of $d$ terms.† The values of the first terms, with Paschen's notation, are as follows :

| $s$ terms. | $p$ terms. | $d$ terms. |
|---|---|---|
| $1{\cdot}5s_2=38040{\cdot}731$ | $2p_1=20958{\cdot}718$ | $3s_1'=11493{\cdot}777$ |
| $1{\cdot}5s_3=39110{\cdot}808$ | $2p_2=22891{\cdot}003$ | $3s_1''=11509{\cdot}498$ |
| $1{\cdot}5s_4=39470{\cdot}160$ | $2p_3=23012{\cdot}015$ | $3s_1'''=11519{\cdot}257$ |
| $1{\cdot}5s_5=39887{\cdot}610$ | $2p_4=23070{\cdot}944$ | $3s_1''''=11520{\cdot}818$ |
| $*1{\cdot}5s_3-1{\cdot}5s_2=1070{\cdot}077$ | $2p_5=23157{\cdot}342$ | $3d_1'=12228{\cdot}051$ |
| $1{\cdot}5s_4-1{\cdot}5s_3=359{\cdot}352$ | $2p_6=23613{\cdot}586$ | $3d_1''=12229{\cdot}816$ |
| $1{\cdot}5s_5-1{\cdot}5s_4=417{\cdot}450$ | $2p_7=23807{\cdot}852$ | $3d_2=12292{\cdot}853$ |
| | $2p_8=24105{\cdot}229$ | $3d_3=12322{\cdot}259$ |
| | $2p_9=24272{\cdot}411$ | $3d_4=12337{\cdot}323$ |
| | $2p_{10}=25671{\cdot}654$ | $3d_4'=12339{\cdot}151$ |
| | | $3d_5=12405{\cdot}233$ |
| | | $3d_6=12419{\cdot}875$ |

* These are the constant difference values previously noted.

The possible number of combinations is thus very large, but not all of them appear in the spectrum. For example, of the 40 possible principal series $1{\cdot}5s-mp$, 30 are actually observed, and there are similarly 30 sharp series; of the possible 120 series of diffuse type, 72 have been identified.

A large number of these series were found to be represented with remarkable accuracy by the Ritz formula : namely the 72 series :

$$\left.\begin{matrix}2p_4\\2p_6\\2p_8\\2p_9\end{matrix}\right\}-md_1'$$

$$\left.\begin{matrix}2p_4\\2p_5\\2p_{7-10}\end{matrix}\right\}-md_1''$$

$$2p_{1-10}\quad-md_2$$

$$\left.\begin{matrix}2p_2\\2p_{4-10}\end{matrix}\right\}-md_3$$

$$\left.\begin{matrix}2p_4\\2p_{6-9}\end{matrix}\right\}-md_4$$

$$2p_9\quad-md_4'$$

$$\left.\begin{matrix}2p_{2-4}\\2p_6\\2p_8\\2p_{10}\end{matrix}\right\}-md_5$$

$$\left.\begin{matrix}2p_2\\2p_5\\2p_7\\2p_{10}\end{matrix}\right\}-md_6$$

$$\left.\begin{matrix}2p_{1-8}\\2p_{10}\end{matrix}\right\}-ms_4$$

$$\left.\begin{matrix}2p_2\\2p_{4-10}\end{matrix}\right\}-ms_5$$

$$\left.\begin{matrix}1{\cdot}5s_2\\1{\cdot}5s_4\\1{\cdot}5s_5\end{matrix}\right\}-mp_6$$

$$1{\cdot}5s_{2-5}\quad-mp_7$$

$$\left.\begin{matrix}1{\cdot}5s_2\\1{\cdot}5s_4\\1{\cdot}5s_5\end{matrix}\right\}-mp_8$$

$$1{\cdot}5s_5\quad-mp_9$$

Owing to the inter-relations between these series, it is sufficient to calculate one limit. The one selected by Paschen was $1{\cdot}5s_5$, and the adopted value was the mean from the four series $1{\cdot}5s_5-mp_{6-9}$. The terms $2p_{6-9}$ thus became known, and it was then possible to calculate $md_1'$, $md_1''$, $md_2$, $md_3$, $md_4$, $md_4'$, $md_5$, $md_6$, $ms_4$, $ms_5$, $1{\cdot}5s_2$, $1{\cdot}5s_3$. Then from $md_2$, &c., the remaining $2p$ terms were found; namely

*Ann. d. Phys., **60**, 405 (1919) ; **63**, 201 (1920).

† In the first paper, four series terms designated $s_1'$, $s_1''$, $s_1'''$, $s_1''''$ were considered to be of $s$ type, but in the second paper these are classed as of $d$ type.

$2p_{1,2,3,4,5,10}$. Thus, all the limits and terms of the above series could be determined, namely:

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $2p_{1-5}$ | $2p_{6-9}$ | $2p_{10}$ | $1{\cdot}5s_2$ | $1{\cdot}5s_3$ | $1{\cdot}5s_{4,5}$ | $3d_1'$ | $3d_1''$ | $3d_{2-4}$ | $3d_4'$ | $3d_{5,6}$ |
| | $3p_{6-9}$ | | | | $2{\cdot}5s_{4,5}$ | $4d_1'$ | $4d_1''$ | $4d_{2-4}$ | $4d_4'$ | $4d_{5,6}$ |
| | $4p_{6-9}$ | | | | $3{\cdot}5s_{4,5}$ | $5d_1'$ | $5d_1''$ | $5d_{2-4}$ | $5d_4'$ | $5d_{5,6}$ |
| | ..... | | | | ..... | ..... | ..... | ..... | ..... | ..... |

These terms being known, the following combination lines were found to exist:

| | | | |
|---|---|---|---|
| $2p_{1-8,10}-1{\cdot}5s_2$ | $1{\cdot}5s_{2,4}-2p_1$ | $1{\cdot}5s_{2,4}-2p_3$ | $1{\cdot}5s_{2-5}-2p_5$ |
| $2p_{2,5,7,10}-1{\cdot}5s_3$ | $1{\cdot}5s_{2-5}-2p_2$ | $1{\cdot}5s_{2,4,5}-2p_4$ | $1{\cdot}5s_{2-5}-2p_{10}$ |

The lines thus indicated were the first lines of additional series, and it was natural to take the limits of such series as $2p_{1-8,10}$, $1{\cdot}5s_{2,4}$, &c. When this was done, however, the terms of the new series did not follow any known type of series formula. With limits calculated independently, from the actual lines, the series were nevertheless of the ordinary type. Two alternatives were therefore open: (1) to preserve the limits indicated by the combination principle and to assert the series to be abnormal; (2) to calculate the limits from the Ritz formula and to abandon or modify the combination principle. In his first paper Paschen adopted the first alternative and proposed new types of formulæ; in the second paper he adopted the second alternative.

Besides the above, the following 28 series were also found:—

| | |
|---|---|
| $A_{1-8,10}-ms_1'$ | $A_{4,6,8,9}-ms_1'''$ |
| $A_{2,4-10}-ms_1''$ | $A_{2,4-8,10}-ms_1''''$ |

The terms $ms_1'$, $ms_1''$, $ms_1'''$, $ms_1''''$ are new and do not arise from the combination principle. There appears, therefore, to be no obvious reason why $A$ should be identified with any of the known terms. Paschen, however, called it $2p$ and again got "abnormal" series. The only justification for this procedure seems to be that the limits calculated by the Ritz formula were identical with those of some of the series for which the above alternatives were open. As before, the second alternative was finally adopted.

The main points in the above arguments may be illustrated by the following numerical calculations:—

$1{\cdot}5s_5=39887{\cdot}61\pm0{\cdot}05$ (from the 4 Ritz type series $1{\cdot}5s_5-mp_{6-9}$)

First lines of $1{\cdot}5s_5-mp_{6,7,8}$ are $\nu=16274{\cdot}02$, $16079{\cdot}76$, $15782{\cdot}38$

$\therefore\ 2p_6=23613{\cdot}59$; $2p_7=23807{\cdot}85$; $2p_8=24105{\cdot}23$

First lines of $1{\cdot}5s_2-mp_{6,7,8}$ are $\nu=14427{\cdot}14$, $14232{\cdot}88$, $13935{\cdot}51$

$$\therefore\ 1{\cdot}5s_2=\text{mean of}\left\{\begin{array}{l}23613{\cdot}59+14427{\cdot}14=38040{\cdot}73\\23807{\cdot}85+14232{\cdot}88=\quad\ {\cdot}73\\24105{\cdot}23+13935{\cdot}51=\quad\ {\cdot}74\end{array}\right\}=38040{\cdot}73$$

First lines of $1{\cdot}5s_4-mp_{6,7,8}$ are $15856{\cdot}57$, $15662{\cdot}31$, $15364{\cdot}93$

$$\therefore\ 1{\cdot}5s_4=\text{mean of}\left\{\begin{array}{l}23613{\cdot}59+15856{\cdot}57=39470{\cdot}16\\23807{\cdot}85+15662{\cdot}31=\quad\ {\cdot}16\\24105{\cdot}23+15364{\cdot}93=\quad\ {\cdot}16\end{array}\right\}=39470{\cdot}16$$

First lines of $2p_4-ms_{4,5}$ are $-16399{\cdot}22$, $-16816{\cdot}67$.

$$\therefore\ 2p_4=\text{mean of}\left\{\begin{array}{l}39470{\cdot}16-16399{\cdot}22=23070{\cdot}94\\39887{\cdot}61-16816{\cdot}67=\quad\ {\cdot}94\end{array}\right\}=23070{\cdot}94.$$

If there be a combination line $1{\cdot}5s_2-2p_4$, its wave-number should be $\nu=38040{\cdot}73-23070{\cdot}94=14969{\cdot}79$.

There is a line in this position, and it is the first member of the series :—

14969·79
27819·95
32490·07
34708·57
35939·3

This series is accordingly designated $1{\cdot}5s_2-mp_4$ where $1{\cdot}5s_2=38040{\cdot}73$. In this form, however, the series is abnormal, and in his first paper Paschen represented it by the formula

$$\nu=38040{\cdot}73-\frac{109694{\cdot}8^*}{\left(m-0{\cdot}0232537+\dfrac{0{\cdot}0746753}{m}+0{\cdot}0612291e^{m/2}\right)^2}$$

If the entire Ritz formula for the series be calculated, however, the limit being regarded as unknown, the limit is found to be 38821·10, and the series is well represented. The relative accuracy of the two formulæ is indicated by the following residuals $O-C$.

| $m$ | | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $\Delta\nu$ | (Paschen) | +0·01 | 0·00 | +5·83 | 0·00 | −3·50 |
| $\Delta\nu$ | (Ritz) | 0·00 | −0·12 | −0·12 | +0·21 | −3·42 |

When the Ritz limit 38821·10 is adopted, the values of the terms for the above lines are 23851·31, 11001·15, 6331·03, &c., and these naturally follow the Ritz formula. If, however, the limit $1{\cdot}5s_2$ (=38040·73) be adopted, then, since 38821·10 =38040·73+780·37, these terms would be decreased by 780·37, and would become 23070·94, 10220·78, 5550·66, &c. These do not obey the Ritz formula, and in order to make them do so they must be increased by 780·37. Paschen actually adopts $1{\cdot}5s_2$ for the limit, and the terms $mp_4$ are calculated accordingly; for comparison with the Ritz formula, he then uses terms "($mp_4$) reduced," which are equivalent to $mp_4+780{\cdot}37$. And similarly for the other series of this character.

Altogether, there are 48 series with the limits thus displaced by about 780 units, 2 with displacements of about 730, 4 with 763, 2 with 40, and 4 with displacements of 10 units. That is, the limits calculated by the Ritz formula differ by these amounts from those indicated by the combinations which give the first lines of the series. The significance of these displacements is not yet understood.

Besides these 60 "abnormal" series, there are the 72 normal series previously indicated.

* This is Paschen's value for the series constant of neon calculated in accordance with the quantum theory.

The following table shows the wave-lengths, intensities, and classification of some of the well-known strong lines of neon, together with the Zeeman effects when known :—

| λ | Int. | Series. | Zeeman type. |
|---|---|---|---|
| 6717·042 | 2 | $1{\cdot}5s_2-2p_5$ | Normal triplet. |
| 6266·495 | 15 | $1{\cdot}5s_3-2p_5$ | ,, ,, |
| 5852·488 | 50 | $1{\cdot}5s_2-2p_1$ | ,, ,, |
| 6074·337 | 10 | $1{\cdot}5s_4-2p_3$ | 3/2 Normal triplet. |
| 5400·556 | 50 | $1{\cdot}5s_4-2p_1$ | 3/2 ,, ,, |
| 6506·527 | 15 | $1{\cdot}5s_4-2p_8$ | |
| 6402·246 | 20 | $1{\cdot}5s_5-2p_9$ | |
| 6334·428 | 10 | $1{\cdot}5s_5-2p_8$ | |
| 5975·534 | 12 | $1{\cdot}5s_5-2p_5$ | |

A second spectrum of neon, developed under the action of a condensed discharge, has been observed by Merton,* but no investigations of series in this spectrum have been published.

## ARGON.

A. At. wt.=39·9 ; At. No.=18.

Two spectra are given by argon. That obtained with the uncondensed discharge has its strongest lines in the less refrangible regions, and is called the "red spectrum," while that developed by the condensed discharge has its brightest lines in the blue, and is called the "blue spectrum."

Rydberg† found that most of the lines between λ4702 and λ2967 in the red spectrum could be arranged in quadruplets having constant separations, and the same arrangement was afterwards found by Paulson‡ to extend to the less refrangible parts of the spectrum. If the first line of each quadruplet be designated $A$, and succeeding ones $B$, $C$, $D$, it results that

$$B=A+\ 846{\cdot}47 \qquad \Delta_1=846{\cdot}47\ \S$$
$$C=A+1649{\cdot}68 \qquad \Delta_2=803{\cdot}21$$
$$D=A+2256{\cdot}71 \qquad \Delta_3=607{\cdot}03$$

Some of the "quadruplets" are incomplete, exhibiting only two or three members, and no simple regularity of intensities is evident. Neither Rydberg nor Kayser and Runge succeeded in tracing anything of the nature of the typical series spectra.

* Proc. Roy. Soc., A. **89**, 447 (1914).
† Astrophys. Jour., **6**, 338 (1897).
‡ Phys. Zeit., **15**, 831 (1914).
§ More accurate determinations of the wave-lengths and separations have since been published by Meggers (Scientific Papers, Bureau of Standards, Washington, No. 414, 1921).

Groups of lines in the blue spectrum, some of them incomplete, were also found by Paulson.* These may be represented by the following expressions :—

$$B = A + 844{\cdot}49 \qquad \Delta_1 = 844{\cdot}49$$
$$C = A + 2455{\cdot}82 \qquad \Delta_2 = 1611{\cdot}33$$
$$D = A + 2605{\cdot}37 \qquad \Delta_3 = 149{\cdot}55$$
$$E = A + 2759{\cdot}34 \qquad \Delta_4 = 153{\cdot}97$$

There are also numerous pairs of lines in the spectrum having the differences $\Delta_1$, $\Delta_2$, $\Delta_3$, $\Delta_4$, or $C-A$, $D-A$, &c.

A preliminary analysis of the spectrum of argon, following the methods adopted by Paschen for neon, has been made by Nissen.†

## Krypton.

Kr. At. wt.=82·9 ; At. No.=36.

The original determinations of krypton lines by Baly‡ have recently been supplemented by some very accurate measurements in the region λ8929-6421 made by Merrill at Washington.§ A first inspection of the latter measures revealed three additional pairs of the type discovered by Paulson.‖ The eight pairs are given by Merrill as follows :—

| λ, Int. | Δν | λ, Int. | Δν |
|---|---|---|---|
| 8776·73 (3)<br>8104·33 (7) | 945·06 | 5870·90 (10)<br>5562·23 (6) | 944·96 |
| 8298·07 (6)<br>7694·53 (8) | 945·00 | 4502·39 (9)<br>4318·58 (8) | 945·06 |
| 8190·02 (6)<br>7601·55 (20) | 944·97 | 4463·71 (10)<br>4283·01 (4) | 944·95 |
| 5879·84 (1)<br>5570·28 (10) | 944·99 | 4453·95 (10)<br>4273·99 (10) | 945·04 |

Paulson has also indicated five pairs having a mean separation $\Delta\nu$ of 4732·9.

Krypton exhibits two spectra, one produced without condenser in the discharge circuit, and a second when the condenser is introduced. The above lines occur in the condensed discharge.

## Xenon.

Xe. At. wt.=130·2 ; At. No.=54.

The sources of data for xenon are the tables of Baly and Merrill, the latter extending from λ9163 to λ5823.

The strongest lines in the red end are 8231·62 and 8280·08, which are believed to be good standards of wave-length in the extreme red.

* Astrophys. Jour., **41**, 75 (1915).
† Phys. Zeit., **21**, 25 (1920).
‡ Phil. Trans., A. **202**, 183 (1904).
§ Sc. Papers, No. 345 (1919).
‖ Ann. d. Phys., **45**, 428 (1914).

Paulson* has drawn attention to four "triplets," having separations $\Delta\nu$ of about 3685 and 760. The intensities in these groups, however, show no regularity, and three of the triplets have the wider separation on the more refrangible side.

An interesting feature of the spectra of neon, argon, krypton and xenon has been noted by Merrill, namely, the tendency of the lines to form large groups occurring in positions which are apparently related to the atomic weights. Merrill photographed the spectra with small dispersion, and the displacement of the groups to the red with increase of atomic weight is thus very clearly indicated. Thus, there are groups beginning at $\lambda$ 5850 in Ne, $\lambda$6970 in A, $\lambda$7590 in Kr, and $\lambda$8230 in Xe. There are comparatively blank spaces on the more refrangible sides of each of these groups. Correspondence between individual lines of the different elements, however, is not clear.

NITON. (Radium Emanation.)

Nt. At. wt.=222·4; At. No.=86.

The spectrum of the radium emanation was first studied by Ramsay, and afterwards more completely by Rutherford and Royds,† and again by Royds.‡ Wavelengths extending from 6079 to 3005 are thus available,§ but there is no record of any attempt to trace regularity in the arrangement of the lines.

* Astrophys. Jour., **40**, 307 (1914).

† Phil. Mag., **16**, 313 (1908).

‡ Proc. Roy. Soc., A. **82**, 22 (1908). Phil. Mag., **17**, 202 (1909).

§ A further investigation of this spectrum over the range $\lambda\lambda$3982 to 7450 has since been made by Nyswander, Lind, and Moore (Astrophys. Jour., **54**, 285, 1921).

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# DESCRIPTION OF PLATES.

## PLATE I.

(1) Arc spectrum of sodium, showing principal, sharp and diffuse series. (Quartz spectrograph.)

(2) Arc spectrum of lithium, showing principal, sharp and diffuse series. (Quartz spectrograph.)

(3) The sharp and diffuse series of sodium, with components resolved. The principal pair, $\lambda\lambda$5896, 5890, is reversed. (Glass spectrograph.)

## PLATE II.

The arc spectra of cadmium, zinc, and magnesium (quartz spectrograph). The triplets of the diffuse and sharp series are marked. There is an impurity of zinc in the cadmium spectrum, and of cadmium in the spectrum of zinc. The series marked "D" in the spectrum of magnesium is the Rydberg singlet series. The line $\lambda$2852 is the first principal line of the magnesium singlet system. The lines marked at $\lambda\lambda$ 3261, 3076, and 4571, are the "resonance lines" ($1S$—$1p_2$) of Cd, Zn, and Mg respectively.

## PLATE III.

(*a*) Corresponding sharp triplets of Zn, Cd, and Hg, showing relative positions in the spectrum, and the relative separations.

(*b*) A fundamental triplet of barium, showing the diffuse character of the lines in the arc in air (lower spectrum), and the presence of satellites in the electric-furnace spectrum at low pressure (A. S. King, Mt. Wilson Observatory).

(*c*) A sharp and a diffuse triplet of calcium compared. The fundamental triplet shown on the plate has separations corresponding with those of the satellites of the first diffuse triplet, which lies in the infra-red.

## PLATE IV.

Arc and spark spectra of the alkaline-earth metals. In each case the arc is below and the spark above. Typical series lines are marked. The reduced intensities of the characteristic arc lines, and the enhancement of the spark lines in the spark spectrum are clearly shown. The increased separations of the arc triplets, and of the enhanced doublets, with increase of atomic weight should be noted, and also the displacement of corresponding lines towards the red. The shorter lines in the spark spectra are due to nitrogen and oxygen. (Thorp-grating spectrograph.)

## PLATE V.

(1) The spectrum of helium between $\lambda$3188 and $\lambda$7066, showing the arrangement of the lines in six series. (The two associated fundamental series are in the infra-red.)

(2) The upper spectrum is that of helium with an ordinary uncondensed discharge, and the lower that obtained with a strong condensed discharge. The latter shows the line $\lambda$4686 of $He^+$ very strongly, while the ordinary lines tend to disappear.

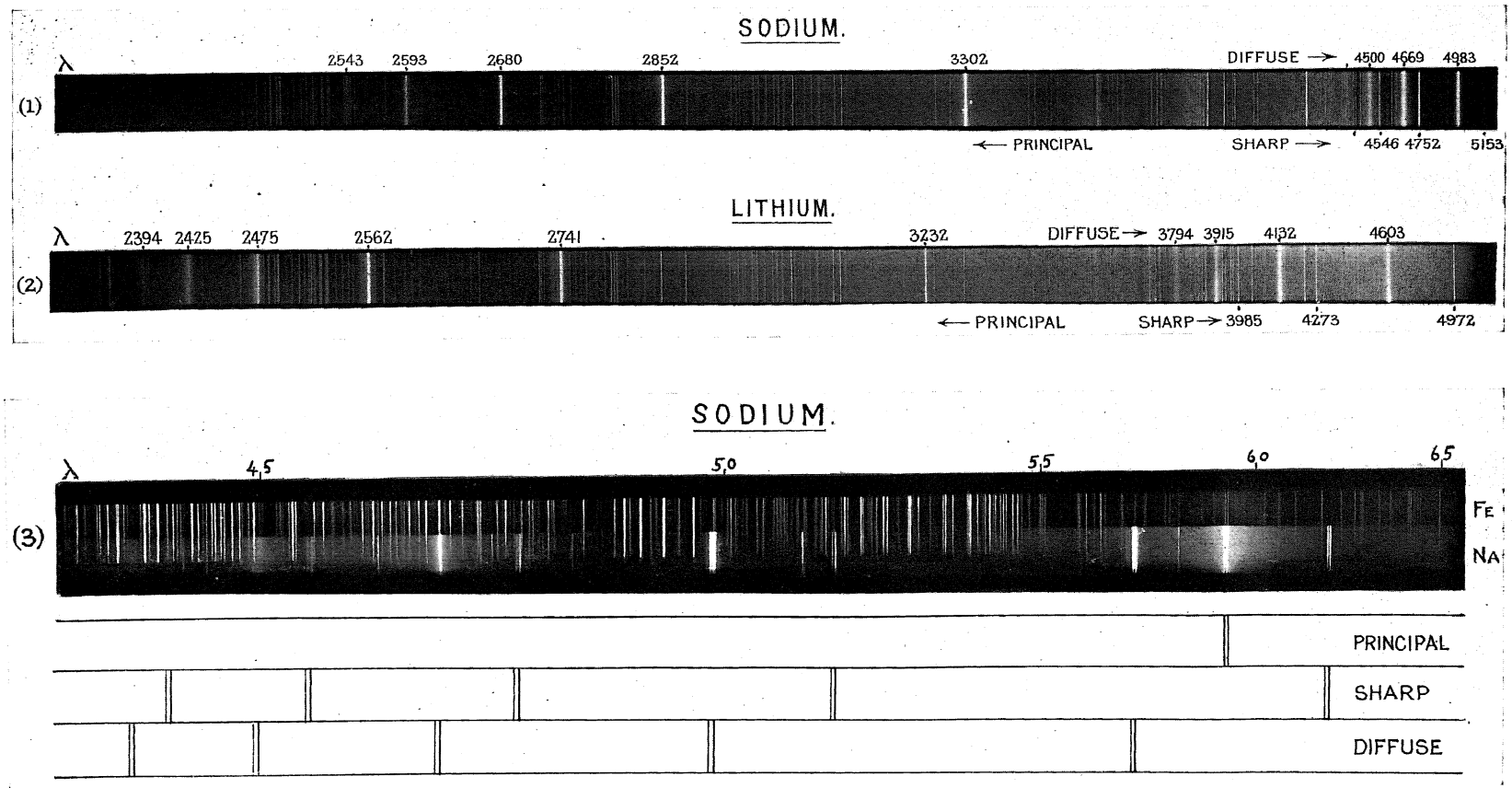



PLATE I.—ARC SPECTRA OF SODIUM AND LITHIUM, SHOWING THE CHIEF SERIES.

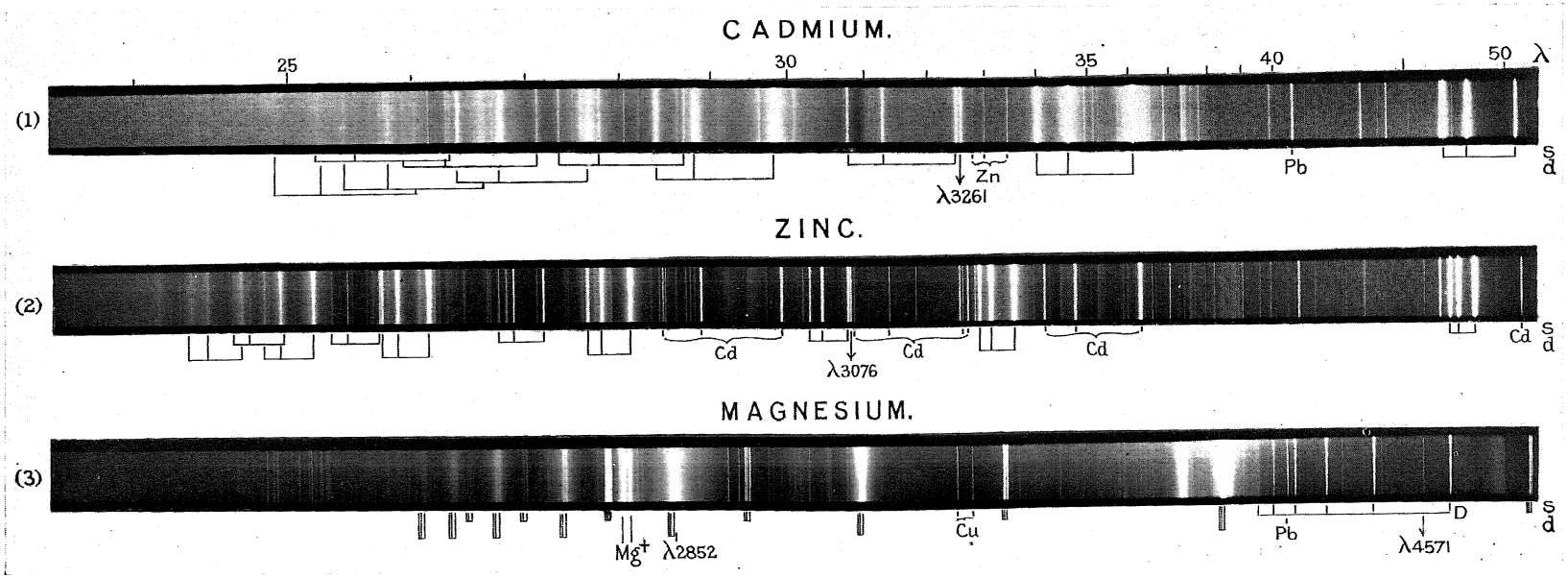
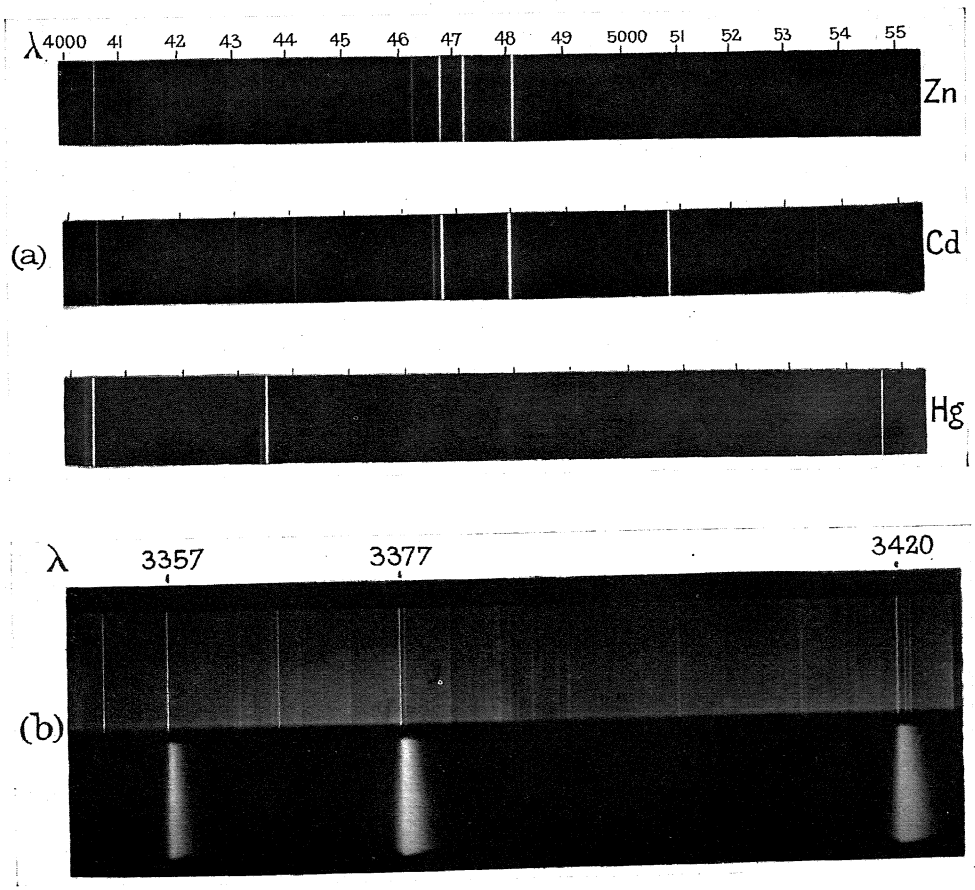



PLATE II.—ARC SPECTRA OF CADMIUM, ZINC AND MAGNESIUM, SHOWING SERIES TRIPLETS.



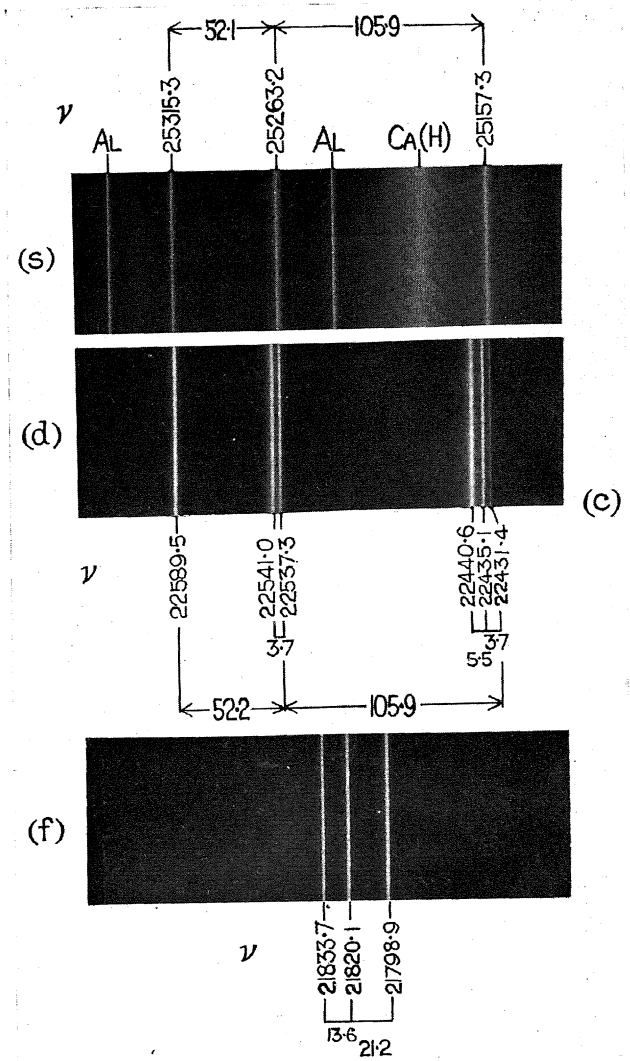




PLATE III.

(*a*) RELATIVE SEPARATIONS OF TRIPLETS OF ZINC, CADMIUM AND MERCURY.
(*b*) SATELLITES IN FUNDAMENTAL TRIPLET OF BARIUM.
(*c*) COMPARISON OF SHARP, DIFFUSE, AND FUNDAMENTAL TRIPLETS OF CALCIUM.

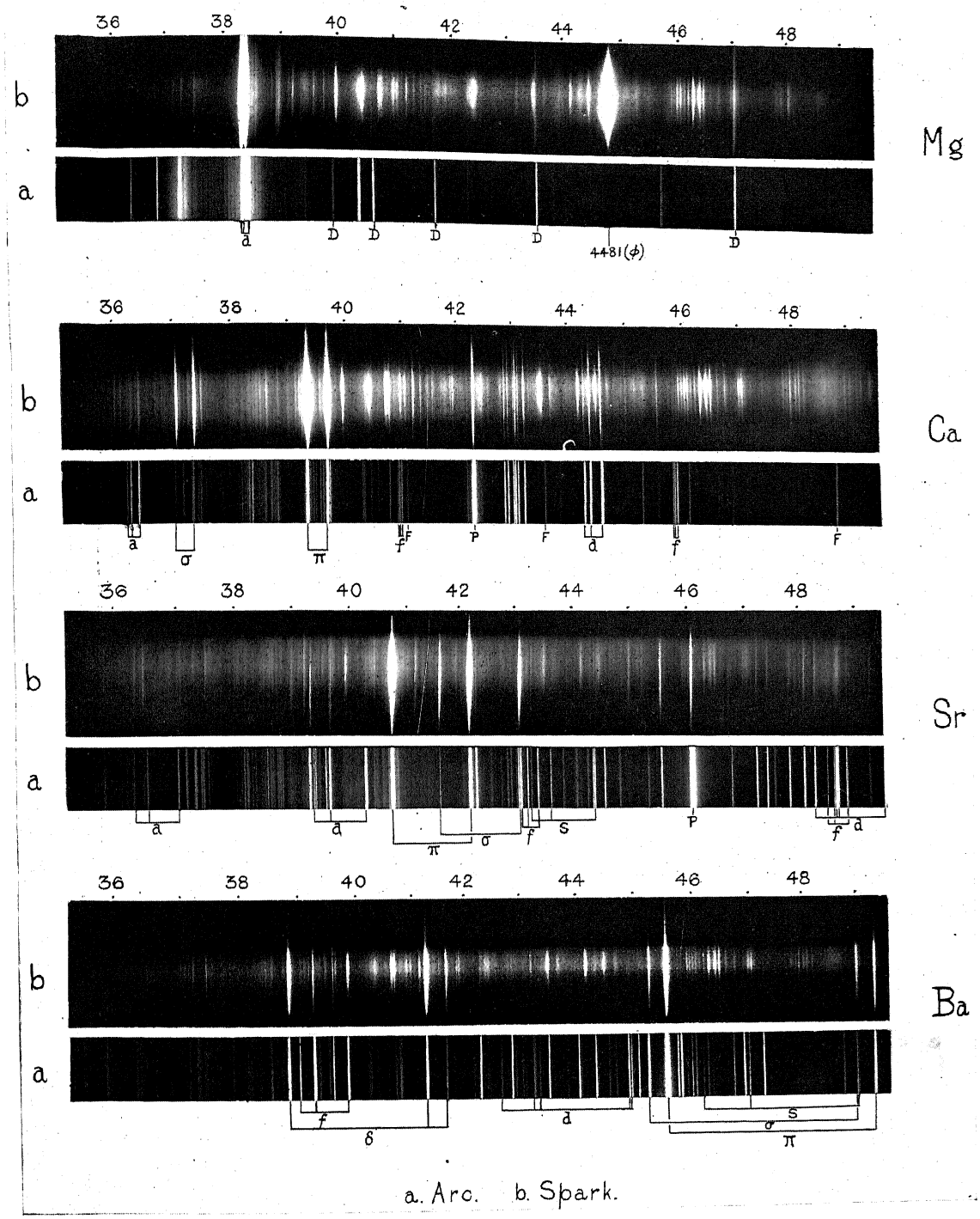



PLATE IV.—ARC AND SPARK SPECTRA OF MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM.

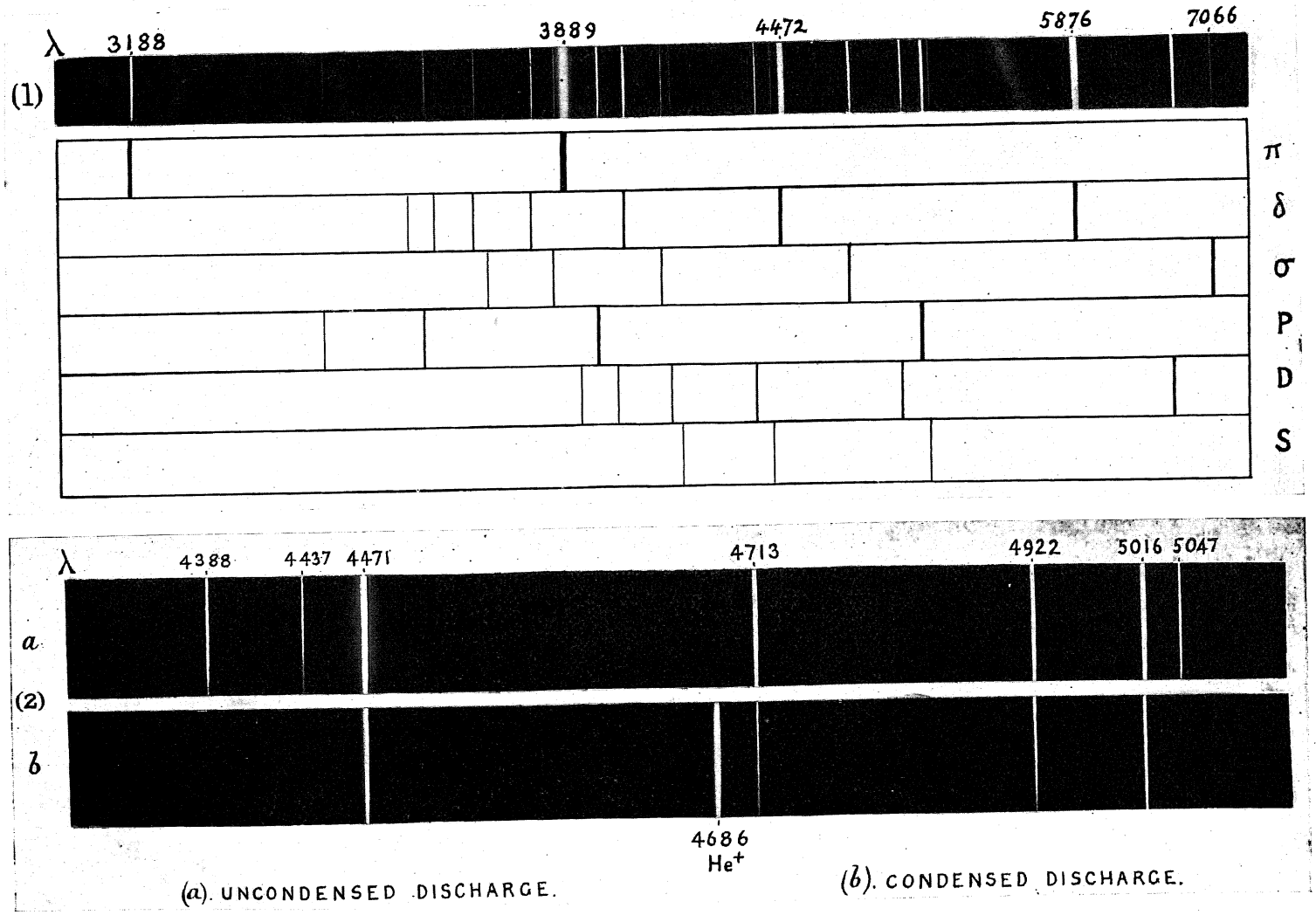



PLATE V.—SPECTRA OF HELIUM AND IONISED HELIUM.